

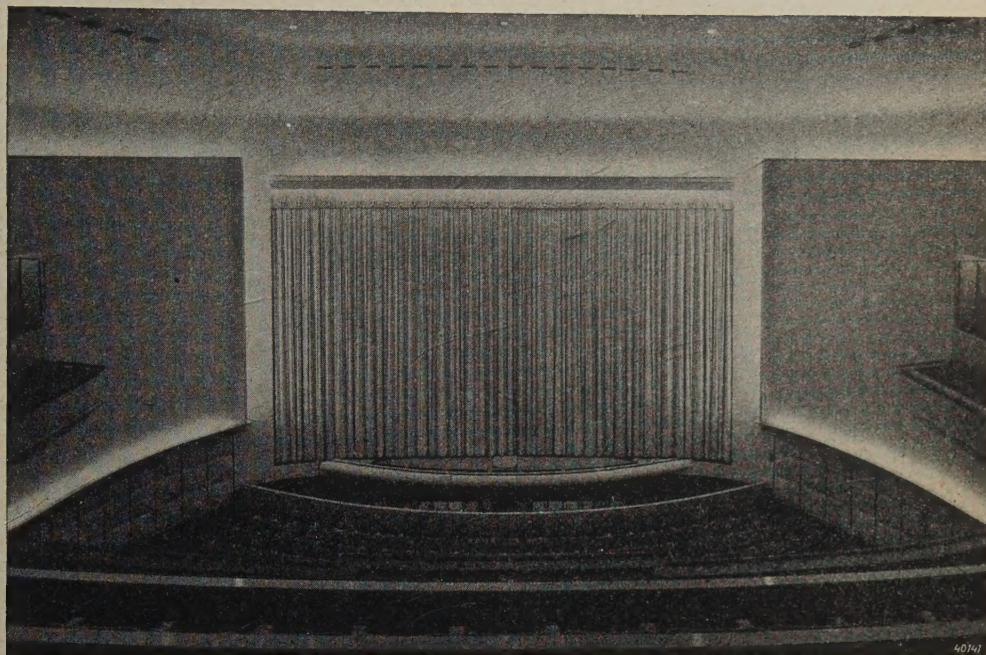
# Philips Technical Review

DEALING WITH TECHNICAL PROBLEMS

RELATING TO THE PRODUCTS, PROCESSES AND INVESTIGATIONS OF

N.V. PHILIPS' GLOEILAMPENFABRIEKEN

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## THE ILLUMINATION OF THE NEW MUNICIPAL THEATRE IN UTRECHT

by L. C. KALFF.

628.972

In connection with the opening of the new Municipal Theatre in Utrecht, a discussion is here presented of the influence on the architecture of the interior exerted by the artificial illumination. The conclusion is reached that in this case illumination and architecture are so intimately related that the building represents a step forward in the progress of illumination architecture.

In visiting the new theatre in Utrecht it is interesting to compare the impression received with that made by older theatres, in order to see what signs can be found of a development in plan, architecture and technical installation. In this periodical we shall confine ourselves to a discussion of the interiors and especially to the problems of illumination and acoustics<sup>1)</sup>.

In this most recent creation of the architect D u d o k, the illumination plays such an important role in the architecture of the interior that it would be impossible to separate light and form from each other. This striking characteristic of the various parts of Utrecht's theatre

points to an important evolution in illumination architecture.

### Several episodes in the progress of the development of theatre illumination

Until 1920 all theatres were in fact illuminated in a way which had become traditional and which was derived from the candles of the oldest theatre halls. This tradition had grown up logically. All the halls were anything but fire-proof, for the curved surface of walls and ceilings necessitated the use of wood; the walls, chairs, floors, everything, in short, was made of wood and covered with cloth. The lighting of the hall had thus to be installed in such a position that

<sup>1)</sup> Cf. the following article by R. Vermeulen.



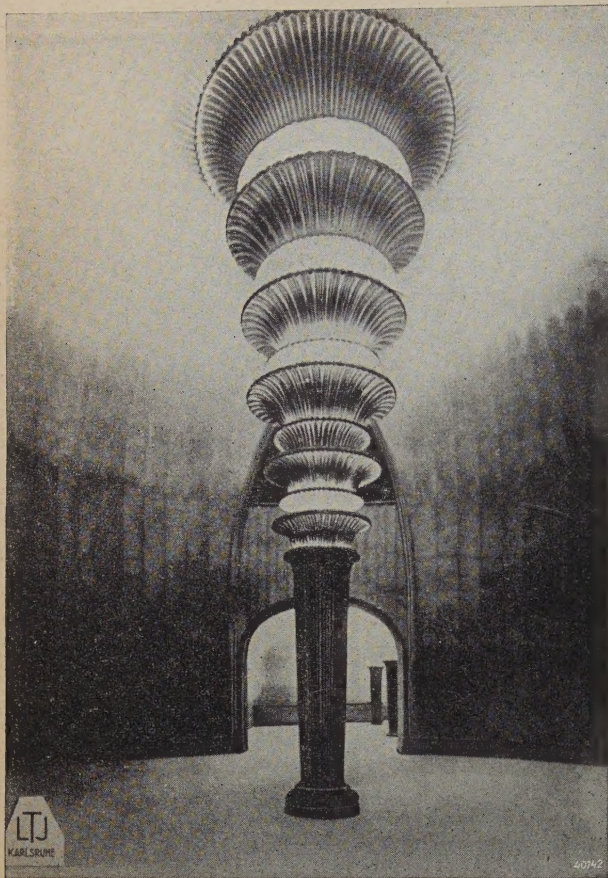


Fig. 1. One of the entrance halls in the „Große Schauspielhaus“ in Berlin, built by architect Poelzig. (The auditorium of the theatre is not typical of such structures, since it is a rebuilt circus building). The picture shows one of the earliest examples of an intimate relation between light and architecture. Especially when it is kept in mind that this building dates from immediately after the world war, the merits of the architect can be rightly assessed.

the flames of candles and oil lamps, and later of gas, offered the least danger of fire. In most cases the position chosen was the centre of the hall, where a monumental chandelier bore the necessary number of light sources. Directly above the chandelier a grating was installed with a large ventilation shaft in the cupola above, in order to carry away the excess heat. As long as electric lighting was still unavailable the chandelier had to be lighted with tapers or candles on long poles, or, before the performance the whole chandelier was lowered with a winch and then lighted. Gas flames were then able to burn very low during the performance, but the oil lamps and candles remained lighted the whole evening.

Some theatres with boxes, like the famous Scala in Milan, had an elaborate system of lighting along the walls, on brackets between the boxes, so that they were easily accessible from the gallery.

Both of these solutions originated from necessity. But although electric light was introduced into most large theatres before 1900, no examples can be found before 1920, where the illumination was given any other than the traditional position.

This illumination had as yet only little influence on the form of the decoration of the hall; it may, however, be assumed that the frequent use of gilded mouldings and leaf-work, like the common use of lustrous textile materials such as silk and brocade, was a result of the dimness of the sources of light. By the use of these materials and also of crystal prisms in the

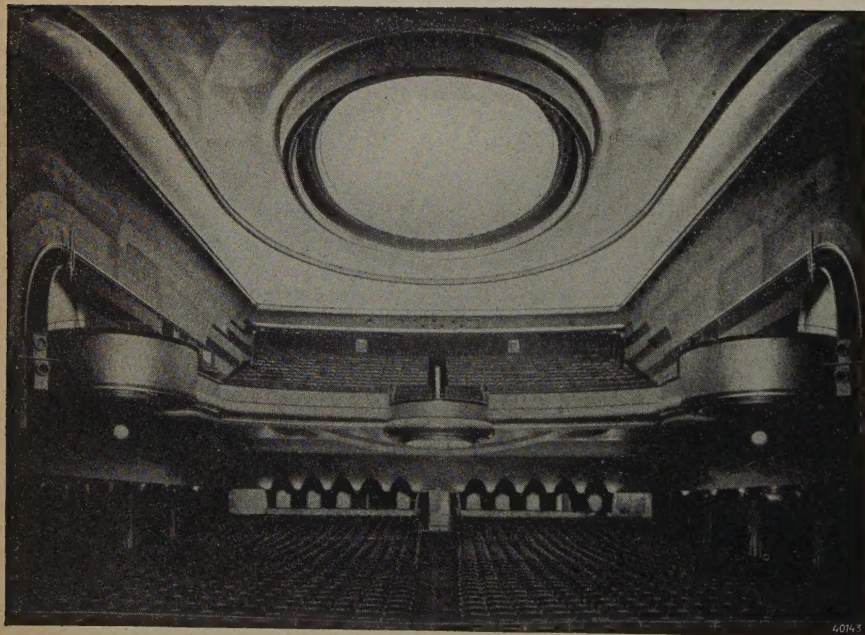


Fig. 2. The great auditorium of Titania Palast in Berlin by the architects Schöpper, Schoenbach and Jacobi.

The new possibilities of building with light have been employed here by the architects on a rather excessive scale, so that the lines of the hall are not organic and the impression now given is that the hall is already no longer modern.



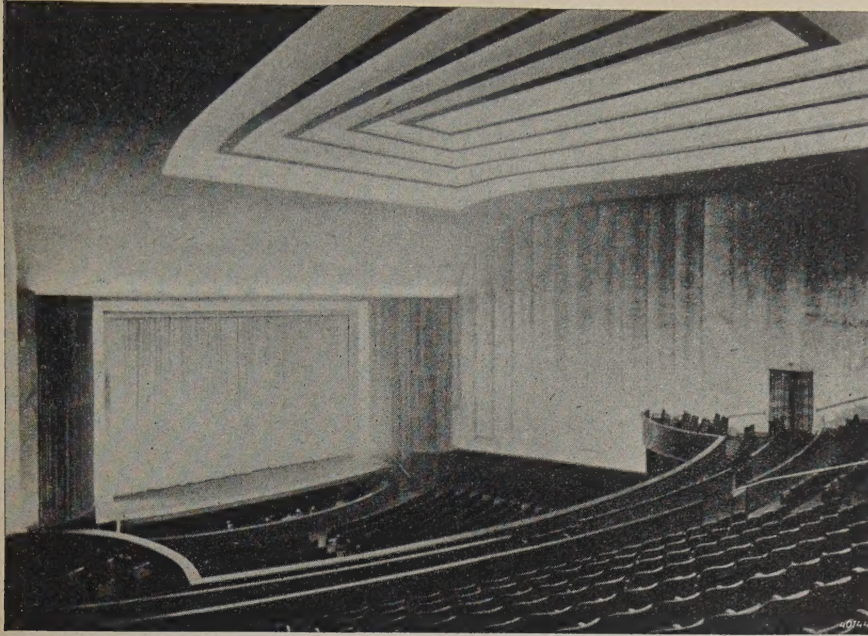


Fig. 3. Theater Lichtburg, Berlin, architect Rudolf Fränkel. The architecture here is much more restrained than in fig. 2. In a restful way the light has here been promoted to the position of the chief decorative motive. Although not all the possible consequences of the new light architecture have been carried through, this hall at the present time is still very pleasing and its lines are certainly not outdated.

chandeliers and of mirrors, the effect of the weak flames of candles and oil lamps was intensified.

While at first the introduction of the electric lamp had little effect on the decoration of the theatre auditorium, this was altered after the world war. People began to go out more and to seek in social entertainment and new impressions to drown their memories of those sad, dark years. In particular, however, it was the cinema which experienced an enormous development. It was in those years that the first huge cinema halls were built, such as Titania Palast in Berlin, Tuschinsky in Amsterdam and the Paramount Theatre in Paris. Originally, because films were still silent, and later because the sound can be amplified many times with loudspeakers, the acoustics of such halls presented less complicated problems to the architect than the acoustics of theatre auditoria. In cinema halls much greater distances between stage and audience can be tolerated than in theatres, and the architect feels less bound to the classic forms and materials of the playhouse.

In the field of illumination a large number of new designs were originated after 1920. The fact that the rapid growth of the film industry furnished the stimulus to this, resulted in an abnormally rapid development (with many excesses), which gradually also affected theatre construction. The architect Poelzig in Berlin, who rebuilt an old circus building into the „Große Schauspielhaus” (see fig. 1), must certainly be mentioned as a pioneer. However, because of its quite exceptional form, this building has not had much influence on the development of the theatre auditorium.

The auditorium of Titania Palast in Berlin (fig. 2) is an example of the redundant new wealth of line which artificial illumination puts at the disposal of the architect. It will now be generally agreed that this redundancy failed to provide pleasing results. The lack of unity between the form and the purpose of the hall, and the unrestrained decorative forms provide evidence that it marked the beginning of a phase of development which still lacked the necessary clarification.

In contrast to this example we may consider the „Lichtburg” (fig. 3) which has many more good architectural qualities. The architect has here confined himself to the use of a single lighting motive which is introduced as the only decoration in the ceiling, on the walls and around the stage opening. These light coves give a balanced and restful division into light and dark of walls and ceiling, while the unity in the decoration gives a pleasing effect.

We wish to point out several features in this hall which will enable us to make interesting comparisons in the discussion of the new Utrecht theatre.

The architect has perceived that a theatre auditorium must in the first place form a frame for the changing scene on the stage. He has therefore avoided the fussy decorations which could be varied by means of coloured lights, which were at that time the fashion. He probably considered rightly that in a hall which is repeatedly visited such expensive and temporary effects soon bore and become worthless. As a matter of fact we know of no hall possessing an installation for three or four different colours



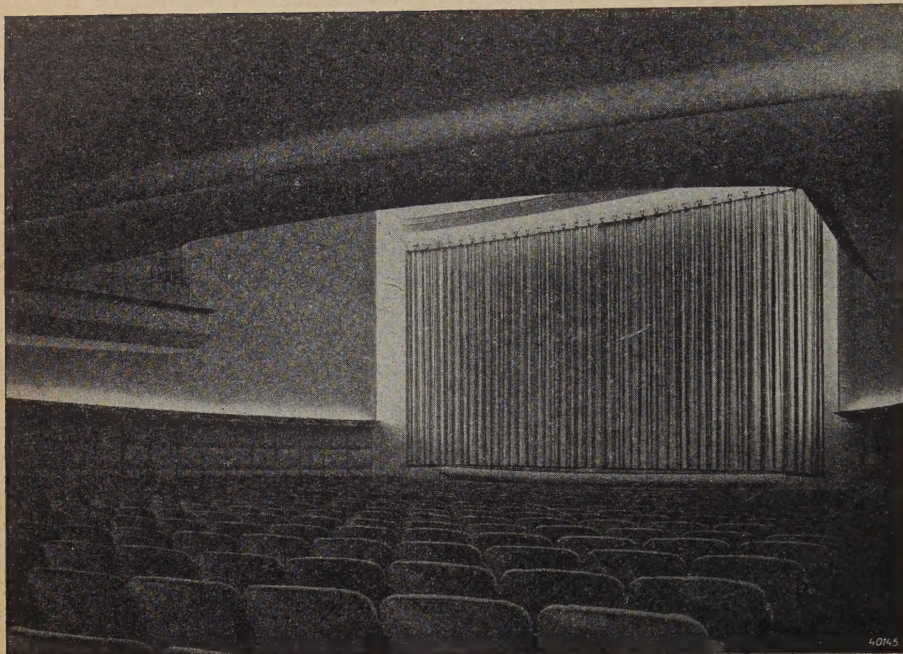


Fig. 4. View of the stage of the new theatre in Utrecht from the rear seats. The whole stage can be clearly seen. The ceiling of the balcony appears high and short due to its upward sloping form. The half-silvered „Cornalux” lamps in the light coves behind the side walls give strong relief to the very light curtain. A difficulty was found to exist in the difference in colour of lamps of different wattage. The light of 100 W „Cornalux” lamps is much whiter than that of show-window lamps „Philinea” lamps or ordinary lamps of 25 W. For this reason the side walls were painted in a slightly warmer tone and the inside of the light cove above the wainscot was made yellow. This produced an appreciable colour contrast between the light on the side walls and the light on the ceiling and the wall surrounding the stage.

of light in which any other than white light was used some time after the opening!

The position of the light coves is here indicated by the division of the hall, but no connection of the coves themselves and the light which issues from them with the shapes of the surfaces

of wall and ceiling is yet noticeable. There is simply a band of light above the wainscot and around the stage opening, and the same element is repeated several times in the ceiling. In this ceiling, however, a different figure could also have been designed with the same construction, and the light from the frame around the stage opening does not fall upon surfaces especially intended to receive it. Here, therefore, there is not yet the intimate relation between form and lighting effect which might be denominated as consistently sustained illumination architecture.

The framing of the stage opening with light is typical. When this decoration is considered, it is found to be illogical. When the lights in the hall are burning the closed stage opening is not the most interesting part of the hall. At that time the audience will be finding their seats, conver-

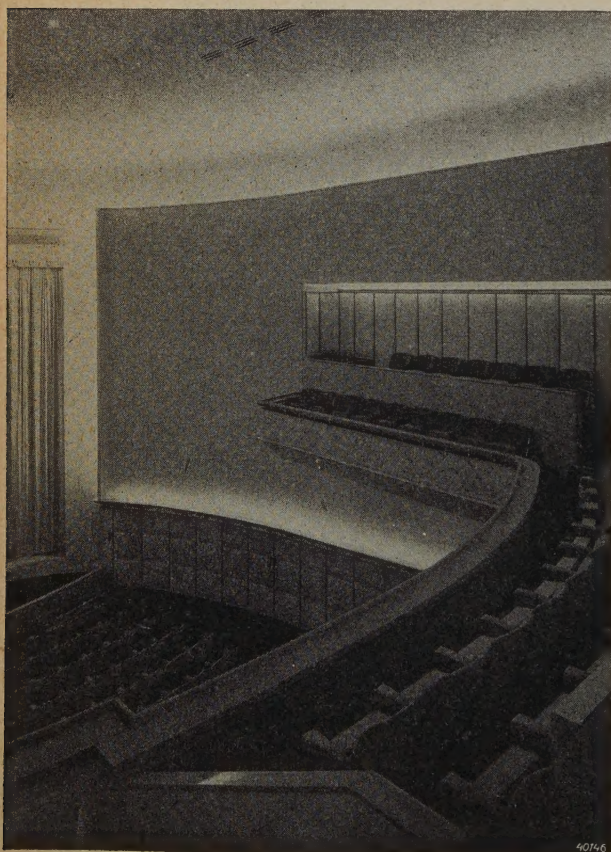


Fig. 5. View of the hall from the balcony. The different arrangements of the illumination are clearly visible here. Attention must be called to the slight unevenness of the ceiling illumination, which could if desired have been avoided by giving the ceiling a completely curved surface. This has, however, been avoided for acoustic reasons (cf. the following article). In practice the uniformity of the brightness of the ceiling was found to be very much affected by the structure of the surface of the plaster. The ceiling is rubbed with silver sand which produces a fine-grained surface. From the point of view of light technology this surface presents the difficulty that it exhibits great differences in brightness according as one observes it in the direction in which the light strikes it or in the opposite direction. This is caused by the innumerable tiny shadows cast by the grains of sand (cf. Philips techn. Rev. 5, 125, 1940).



sing with each other or looking about the hall for acquaintances, etc. But if the attention is to be focussed on the stage, as it were, to increase the anticipation, the light from the above-mentioned frame ought to shine upon the curtain so that its beautiful material and rich drapery constitute an ornament to the wall. This has not been done, however, and the light is directed away from the curtain. And when the hall is darkened and the footlights or the projection apparatus are turned on, the light frame of the most interesting part of the hall must also be darkened !

### Lighting of the Utrecht theatre auditorium

We shall now proceed to the discussion of the auditorium of the new Utrecht theatre, since this is certainly the most important part of the whole building, and since the auditorium discussed above furnishes points of comparison chiefly with this auditorium. We are aware of the fact that in doing this we are not doing full justice to the merits of the architect, because one of the good qualities of this building is the way in which the visitor, moving through the successive rooms and passages, each with its own proportions and atmosphere reaches a climax in the auditorium. We shall, however, speak of that later.

Above the wainscot of padded white artificial leather with gilt borders the hall is entirely in cream-white plaster. The colour scheme is extremely simple. The only colours present are those of the dark brown carpet and the striking brick-red velvet upholstery of the seats. The shape

of the hall is such that every seat has an absolutely free view of the stage and that speech as well as music is excellently heard everywhere in the auditorium. In our opinion this is of more value than the intimacy lost by the arrangement, which could have been avoided by building two, less deep galleries, which, however, always contain a number of poor seats. The lighting here forms an integral part of the line and decoration of the hall, and in our opinion this is an extremely important advance in the art of interior decorating.

The side walls, curving gently toward the stage give the impression of being free standing shells from behind which light shines out. This light falls on the ceiling and thus takes away its heaviness, it also falls upon the gleaming curtain of the same colour as the wall and thus gives interest to that part of the wall even when the curtain is closed (*fig. 4*). The side walls are relatively dark, but they therefore form as it were the fixed surface behind which the widening space recedes (see *fig. 5*).

The ceiling under the large balcony is treated in the same way. It gives the impression as if a free thin shell were suspended under the back of the balcony, from behind which the upward sloping front part of the ceiling of the balcony is lighted. This removes all the heaviness of this large surface, and there is no sense of depression in this lowceilinged part of the hall. The back part of the ceiling is pierced by five large flat domes, so that there also the impression is given that the lighted surface recedes far away above (see *fig. 6*).

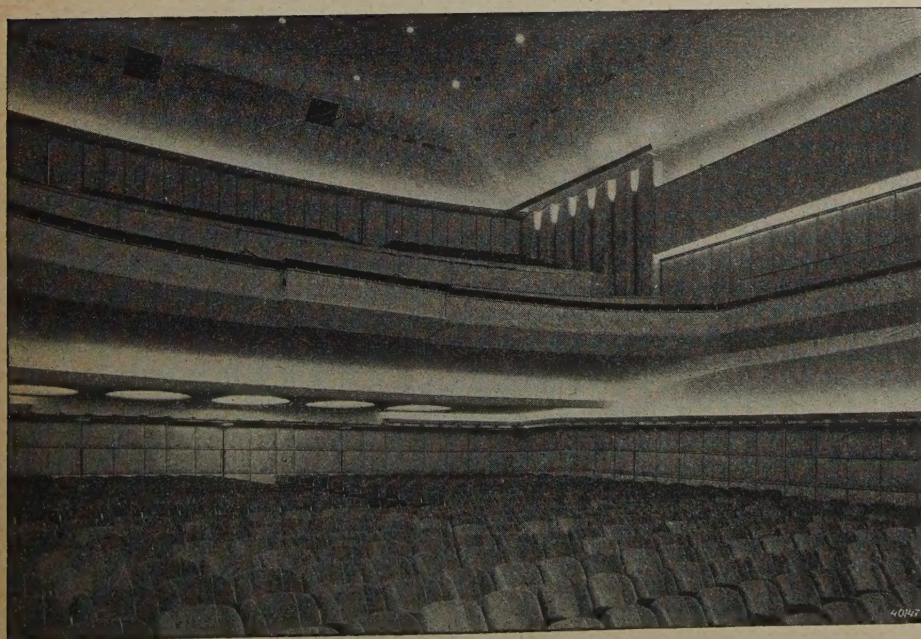


Fig. 6. View from the stage into the auditorium. Attention is called here to the form of the ceiling under the balcony which gives the appearance of a thin free-hanging shell in which circular holes are pierced and above which the upward sloping, brightly lighted ceiling of the balcony is suspended. In the ceiling of the auditorium may be seen the regularly spaced small holes through which direct light is thrown upon the audience.



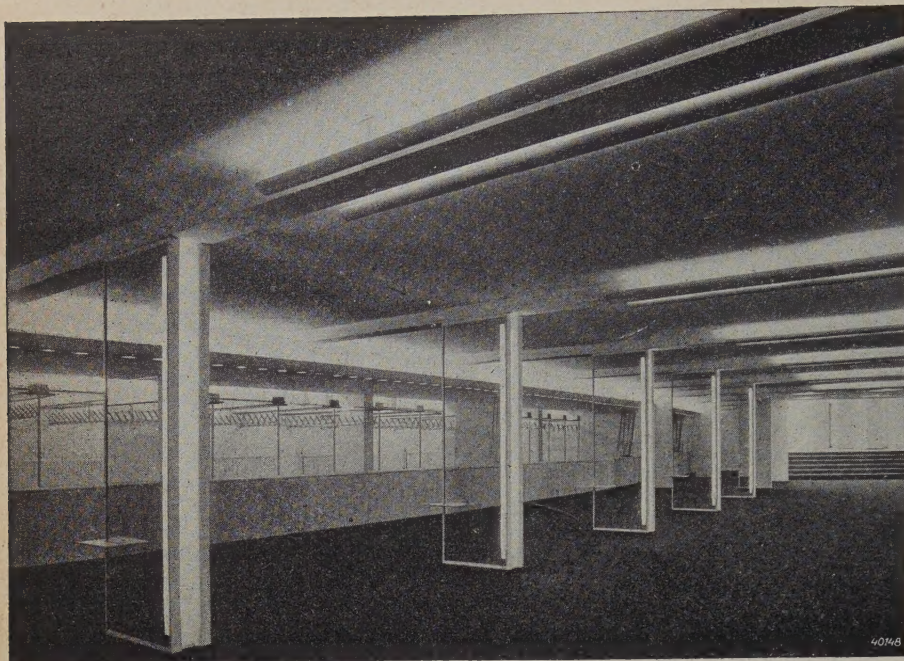


Fig. 7. The cloak-room is lighted entirely with indirect light from light coves above the counters and attached to the beams of the ceiling. The latter prevents an unnecessarily heavy impression being given by the beams. The illumination with the vertical mirrors, which also take away the heaviness of the columns which they hide, forms a pleasing accent.

It would lead us too far if we were to discuss many more of the details of this hall, but we hope with the help of the photographs to have

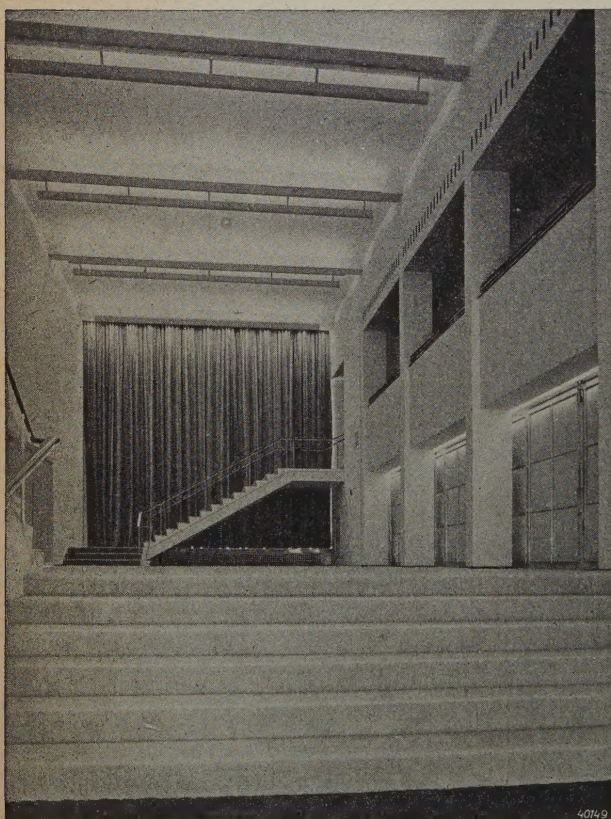


Fig. 8. Coming from the low-ceilinged cloak-room one enters the lofty hall which is lighted in the same simple manner as the cloak-room. Everywhere use is made of special lighting of the hangings to bring out the beautiful effects of the rich materials used.

shown that the work as a whole would be absolutely unthinkable without the light. Not only does it everywhere provide the necessary illumination, but it accentuates the distances between the different surfaces, provides an interesting variety of light and dark, it slides gently over the smooth curves of the padded wainscots, conjures up rich gleams in the folds of the stage curtain and falls unsuspected from the small openings in the ceiling on the gowns and jewels of the audience, so that also there is no lack of vivacity.

The features indicated show the progress which has been made since the time of the examples previously mentioned. The builder uses light as a building material, no moulding, surface or colour is chosen before he has taken into account how the light will fall upon it and how therefore it will be seen.

We would by no means claim that this is the first example of which this may be said, on the contrary, we here see a growth and a continuation of the work of others. This piece of work is a link in a chain which will undoubtedly become longer in the future, and in which works of greater perfection will occur. In this connection it is instructive to consider the work of Bijvoet in the auditorium of the theatre „Gooiland” in Hilversum, which exhibits the same principle in a less fully achieved form and which certainly must have constituted an example to our architect in many respects.

#### **Illumination of the other parts of the theatre**

When the other parts of the theatre are stu-



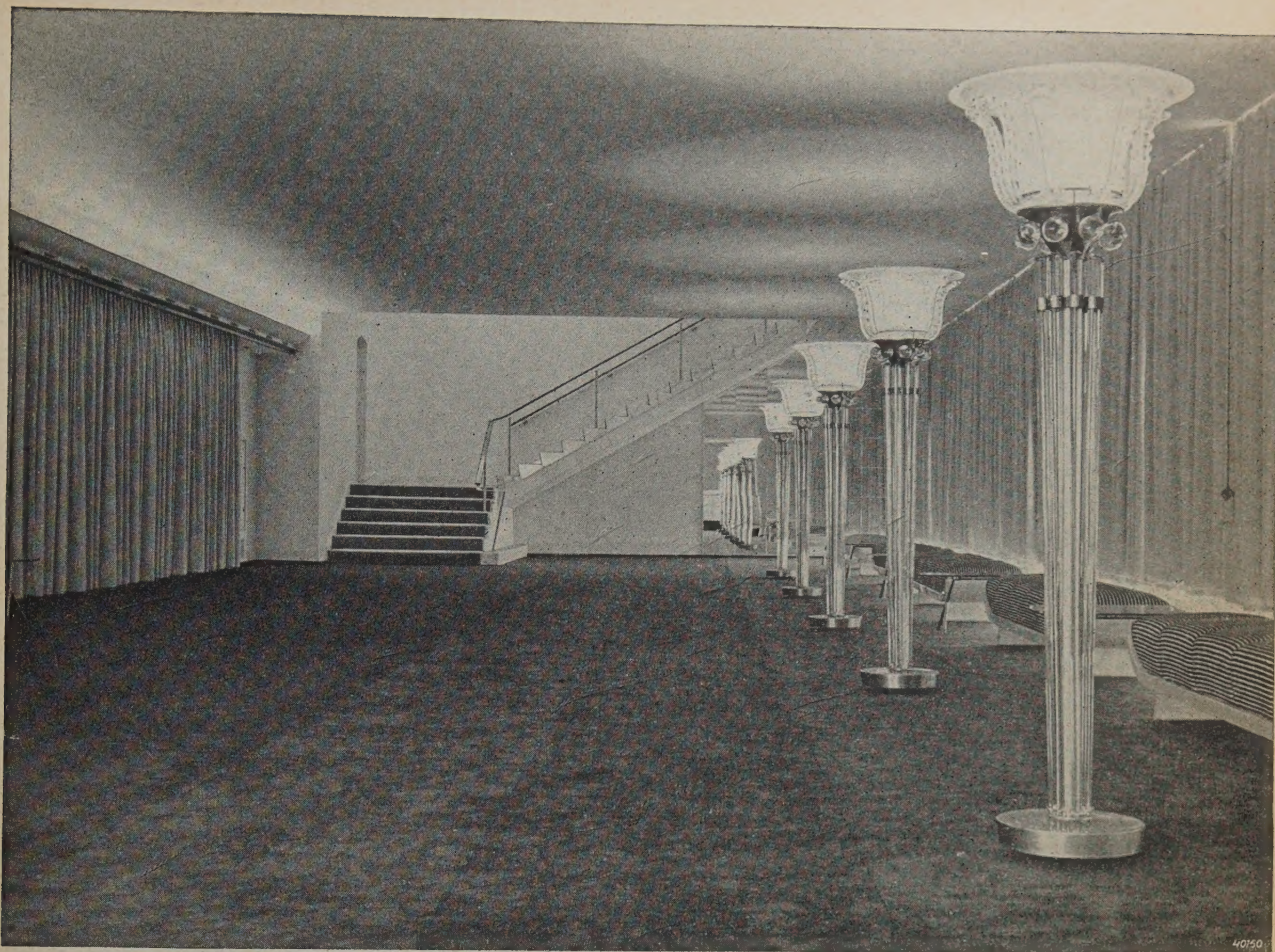


Fig. 9. Through wide doorways the foyer for non-smokers can be entered directly from the auditorium. Here there is a unilateral indirect lighting installed along the side nearest the auditorium, while five monumental glass lamps by Copier of Leerdam, in addition to the indirect lighting *via* the ceiling, give the necessary direct light which is indispensable for a festive atmosphere in such a hall.

died, it first strikes one that no space has been wasted in corridors, and that due to the fact that all the rooms open directly into one another, each room has a well considered relation to the succeeding one. The low-ceilinged cloak-room (*fig. 7*) has an indirect lighting which indeed makes the ceiling less impending but, nevertheless, emphasizes its horizontal character. A pleasant contrast is obtained by the vertical line of the lighting of the mirrors. The cloak-rooms proper can be closed with curtains which are lighted by a long row of holes in the under side of the light cove. This makes this part of the building a pleasant promenade during the intermission.

Passing through the cloak-room, up a short stairway one enters the lofty hall preceeding the auditorium (see *fig. 8*), which forms a surprising climax. The ampitheatre of the auditorium, the restaurant, and the foyer are connected with the hall by means of freely hanging staircases, so that this hall is as it were the

traffic hub of the building. The simple indirect lighting enhances the appreciation of the more studied light decorations in the adjoining rooms.

In the first place we must mention the foyer for non-smokers (*fig. 9*) with the beautiful standard lamps by Copier of Leerdam. Above this is the smokers' foyer and adjoining it the restaurant, which is also accessible directly from the street for the daily clientele (*fig. 10*). In this hall, besides the clever lighting with high glass ornaments in small domes, the beautiful lighting of the curtains is striking, which when it is dark outside and the lovely view of the Dom can no longer be enjoyed, forms a vital substitute for it.

The lighting of all these rooms separately formed only a part of the project. It will be clear that because there is such direct connection between them, the lighting of the different rooms, as far as system, colour and intensity are concerned, must be harmonious, while at the same time the necessary variety must also



be provided. Thus in the room where the public itself is the chief interest, as in the café and the foyers, there is a more generous use of direct

architect and our lighting technologists. Many experiments were tried and many details designed to achieve the desired results. This collabora-



Fig. 10. In addition to the lighting by three rows of half indirect glass ornaments in white plaster domes the restaurant also possesses a very fine curtain illumination which gives to this not very large room a certain grandeur which is very pleasing.

light, while in the theatre the lighting serves primarily to accentuate the hall as back-ground and frame.

It will be understood that all these light effects necessitated years of collaboration between the

tion has always given us the greatest satisfaction.

In the text under the figures we have given various practical details and mentioned certain experience gained which seemed to us to be of importance to the technologist.



# THE ACOUSTICS OF THE AUDITORIUM OF THE NEW THEATRE IN UTRECHT

by R. VERMEULEN.

534.84

In this article the influence is discussed of acoustic considerations in the design of the theatre auditorium in the Municipal Theatre which has recently been opened in Utrecht. At frequencies in the neighbourhood of 500 c/s a reverberation time of approximately 1.2 sec was measured, which agrees with what was expected theoretically.

In conjunction with the foregoing article on the illumination of the Utrecht Municipal Theatre, we shall here discuss the extent to which the requirement of good acoustics has affected the design of the auditorium, a subject about which we were permitted to exchange opinions with the architect W. M. D u d o k at an early stage of the planning. These considerations constitute a constructive application of the general principles of the acoustics of auditoria about which a series of articles has already appeared in this periodical<sup>1</sup>).

## The shape of the auditorium

The ideal situation would be that, in which every member of the audience receives the words directly from the lips of the speaker on the stage. In open-air gatherings where there are no reflecting walls experience has, however, shown that this is only possible over a very limited distance. This distance is found to become much greater when the speaker is placed on a platform high above the public. The sound waves experience great attenuation as they pass over the heads of the hearers, since the wave length for audible sound is of just the same order of magnitude as the dimensions of the heads. The sound waves are therefore refracted toward the spaces between the hearers and are there strongly absorbed. It is thus easy to understand that the sound is much more attenuated at some distance from the speaker, than would follow from the square law for the propagation of sound in space.

The solution of this difficulty for an open-air gathering, namely of placing the speaker high above his audience, cannot be applied in a theatre auditorium, since in that case the stage could not well be seen. It is, however, possible apparently to provide the speaker with this favourable position by causing his voice to be reflected at the ceiling. This reflecting surface should then be given such a form that the sound is distributed as fairly as possible over the whole audience.

If in the different designs for the shape of the ceiling the path of the sound waves is now drawn in, it is quickly noted that it is undesirable

to have the ceiling slope upward from front to rear, which would be architecturally, the logical method of making room for the balcony. The sound in that case would be thrown mainly into the back of the hall, which of itself would be an advantage if it did not occur at the expense of the middle section. As in many cases, it was also found that in the design for the Municipal Theatre a horizontal ceiling furnished favourable results, since it provides the middle of the hall as well as the balcony with adequate sound.

In *fig. 1* the path of the sound rays is drawn in the main cross section of the auditorium, with the angles between successive rays being taken equal to  $5^\circ$ . The beams lying between these rays for directions of sound which do not deviate too greatly from the horizontal, will then all contain equal acoustic power and the intensity is thus inversely proportional to the surface upon which a given beam is incident.

It is obvious that the front rows receive adequate sound, not only because of the short distance, but also because of the fact that the position of the speaker is relatively high above them. For the sound which is reflected by the front part of the ceiling and which if the ceiling were horizontal would be thrown on the front rows of seats, a more useful employment can be found by giving this part of the ceiling a certain slope. The space under the balcony deserves first consideration in this matter since it receives nothing from the horizontal part of the ceiling. Since it is only the slope and not the position of the reflector which is under control, it was only possible to direct a small part of the sound into this space, the remainder is received by the audience on the balcony. In order, nevertheless, to capture as much sound as possible under the balcony the opening of this space was made as high as was compatible with other requirements, while the lower side of the balcony was given such a shape, that the incoming sound was conducted downwards upon the audience. It is scarcely permissible to speak of a reflection in the case of such an almost tangential incidence, since it is here actually the refraction of the sound which predominates.

The corner between rear wall and ceiling

<sup>1</sup>) Philips techn. Rev. 3, 65, 139 and 363, 1938.



always forms a dangerous point, since when the surfaces are mutually perpendicular the rays are there reflected back to the stage parallel to their path of incidence<sup>2)</sup>. In general, it is true, it is desirable that the players receive sound back from the hall in order that they should not obtain the impression that the hall is difficult to play to. This reflection, however, was unsuitable for the purpose because the long distance ( $2 \times 26$  m) which the waves must cover would produce such a retardation that the sound would be heard as an echo. Therefore at the rear of the ceiling there is a section with a slope such that the sound falling upon it is reflected to the balcony.

In the case of the other rays also, care must

be taken that no echo may be formed due to too great time differences. In the front of the hall the time difference is only  $13/330$ , i.e. about  $1/20$  sec, which is quite permissible.

While in the case of the longitudinal cross section the form of the ceiling was for the most part determined by the acoustic requirements, in the design of the transverse cross section the architect may allow other considerations, for example those connected with illuminating technology, to be the determining factors. Many variations are possible since the only condition to be fulfilled is that the sound shall be uniformly distributed over the audience and that it shall not be thrown against the side walls, since otherwise it covers longer distances and a longer reverberation results.

In the case of the form chosen by the architect a slight curvature of the ceiling concentrates

<sup>2)</sup> Compare also the function of a mirror, which has been described in Philips techn. Rev. 5, 335, 1940.

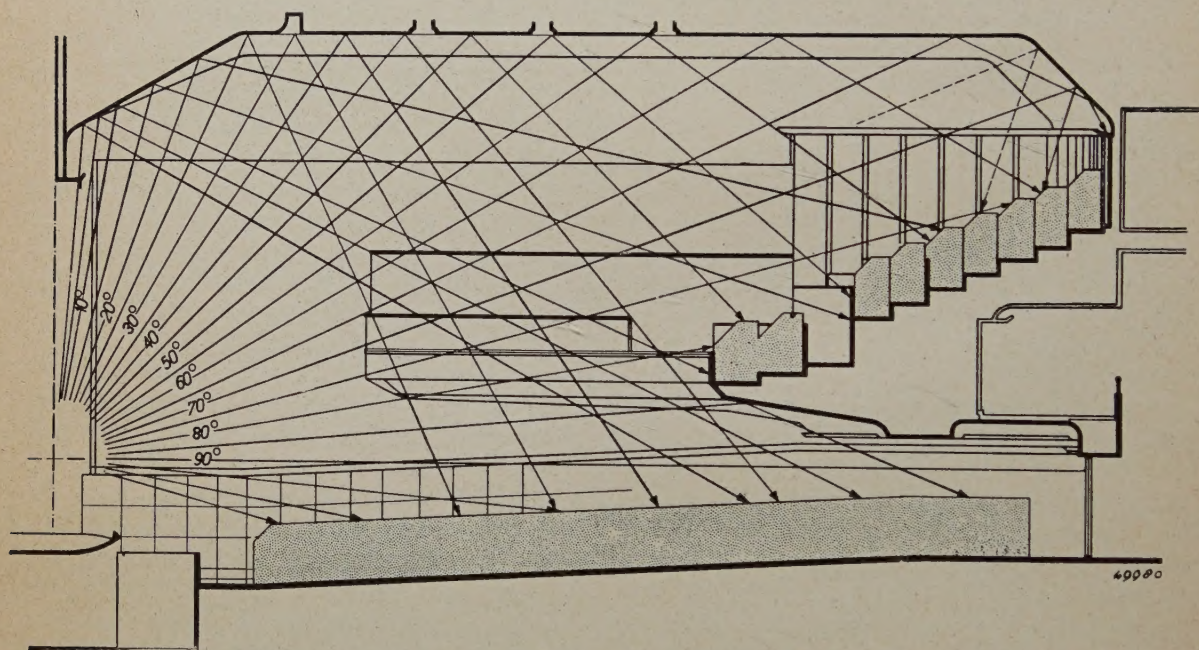


Fig. 1. Longitudinal cross section of the theatre auditorium in Utrecht.

The path of the rays of sound is drawn for sound from a source placed in the opening of the stage wall. From the surface covered by the beam an impression can be obtained of the intensity to be expected. The ray indicated by a broken line, which is only added to make the path of the rays clearer, must be left out of consideration in estimating the distribution of intensity. The space occupied by the audience is shaded. The beam between

105° and 100° falls upon the first 2 m of audience,

100° and 95° falls upon the following 4-5 m of audience,

95° and 90° falls upon the remaining 11 m of audience,

90° and 85° falls upon the underside of the balcony and thus reaches the back rows,

85° and 80° falls upon the front edge of the balcony and is fairly diffusely reflected,

80° and 75° as direct sound, reaches almost the entire balcony,

75° and 60° falls, partly *via* the ceiling, into the back of the balcony,

60° and 45° serves the front of the balcony *via* the ceiling,

40° and 25° falls upon 7-20 m in the middle of the auditorium,

25° and 10° is reflected to the balcony by the oblique part of the ceiling,

10° and 5° reaches the audience under the balcony.



the greater part of the sound on the audience, while the cutting off of the corners directs the sound which would otherwise reach the side walls to the outermost rows of seats (*fig. 2*).

theless be made that it may also be used for music. The immediate direction of the sound on the audience, necessary for a theatre auditorium, makes music sound dry and sharp, since

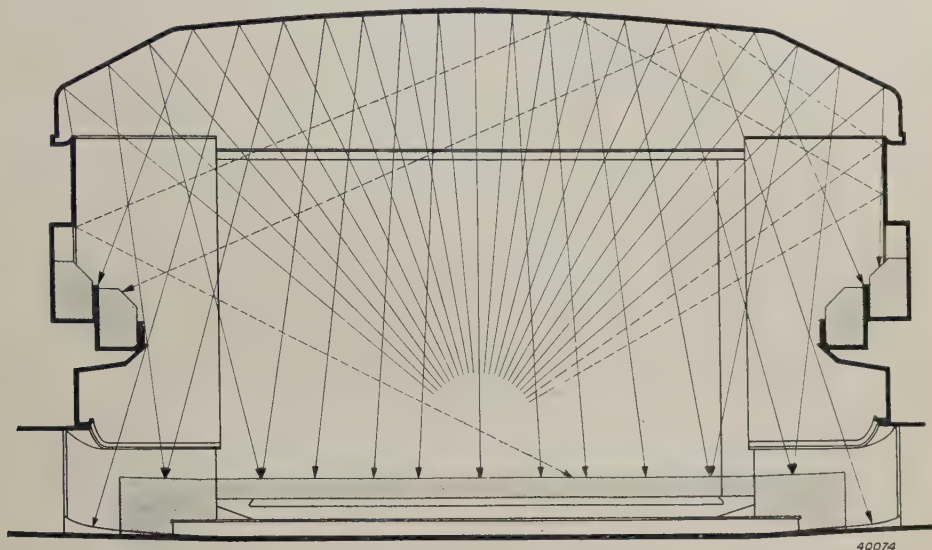


Fig. 2. Transverse cross section of the theatre auditorium in Utrecht.

The source of sound is considered to be in the same place as in *fig. 1*, and the figure shows the reflection of the sound rays by the ceiling. The vaulted part gives a slightly spreading beam upon the audience. The rays which would fall upon the walls after reflection are reflected into the auditorium by the sloping parts of the ceiling.

The path of a few rays which fall directly on the side walls is also shown by dotted lines; these furnish no effective contribution, but will go to make up the reverberation. For the rays drawn the intensity provided can be approximately estimated as in *fig. 1*. This is not the case for the rays not drawn which are directed immediately toward the audience. In *fig. 1* the rays travel in the plane of the drawing, in *fig. 2*, however, they are projections; the source of sound lies far behind, and the receptive audience in front of the plane whereas the rays are reflected at the walls. Therefore beams of rays with equal intensity would have to form very different angles in the drawing.

These beams of sound will be of especial advantage when the speaker does not stand exactly in the centre of the stage and the sound after reflection at the middle section of the ceiling would just miss reaching the rows of seats on the same side as the speaker.

### Reverberation time

In addition to the distribution of the sound which has been reflected once and which provides the chief contribution to intelligibility, the remaining sound, the reverberation, must also still be considered: on the one hand the reverberation time, especially in the low tones, must not be too long, since otherwise, as for instance in a church, the intelligibility decreases, and on the other hand it may not be too short since this produces an uncomfortable feeling and music suffers in quality. Although a good theatre auditorium will never be at the same time an ideal concert hall, the requirement must never-

due to their long wave length the lower tones are much less easily directed. It is therefore desirable that the reverberation should here provide an amplification and should last longer for low tones than for the intermediate region of tones. Since the absorption of most materials increases with the frequency this requirement is automatically fulfilled. The increase in absorption with increasing frequency is even greater than would be expected, so that it still remains necessary to take measures for the sufficient absorption of the bass tones. The plan of the architect of covering the part of the walls within arm's reach from the floor with padded artificial leather seemed to be extraordinarily suitable for this purpose. This covering is not porous and will not therefore absorb high frequencies to any extent. For slower vibrations, however, with the layer of air behind it, it causes the occurrence of a resonance which is damped by the padding.

In general the average value of the reverbera-



tion time in a theatre auditorium gives little cause for anxiety if only the height of the hall is correctly chosen. The absorption of the sound takes place chiefly by the audience, whose absorption coefficient closely approaches 100 per cent. In the plan for the Municipal Theatre the surface area of the balcony was somewhat less than one half of that of the floor of the hall. If we represent this latter quantity by the letter  $S$  the height by  $H$ , then the volume of the hall is  $V = H \cdot S$ . For the absorbing surface of the audience we calculate with the value  $S$  in the hall and  $0.4 S$  on the balcony, and add another  $0.2 S$  for the absorption by the walls, etc. The desired reverberation time was estimated to be 1.2 sec on the basis of various data. Then from the wellknown formula of Sabine for the reverberation time:

$$T = 0.16 \frac{V}{A},$$

where

$V$  = volume of the hall in  $\text{m}^3$ ,

$A$  = absorption of the hall in  $\text{m}^2$  of equivalent open window surface area we find the following value for the height of the hall:

$$H = \frac{V}{S} = \frac{TA}{0.16 S} = \frac{1.2}{0.16 S} (S + 0.4 S + 0.2 S) \\ = 12 \text{ m},$$

which was indeed chosen by the architect.

In a consideration of the different parts which contribute to the absorption it strikes one immediately that the audience furnished by far the greatest share. This has the disadvantage that an incompletely filled house would have a considerably longer reverberation time, and an empty house would even have eight times as long a reverberation time, i.e. 9.6 sec.!

Increasing the absorption of the walls would of course make the influence of the audience relatively smaller, but at the same time it would very much decrease the reverberation time unless the hall were made much larger,

which would not only be an expensive solution but one which would be unsuitable from the point of view of intelligibility. A much better solution is to upholster the seats in such a manner that they can take over the function of the absent audience, but are relieved of their absorbent function by the audience which is present.

The measurement of the reverberation for the empty auditorium already gave the desired value of 1.2 sec, from which the conclusion may be drawn that the chairs actually do perform the part intended for them satisfactorily. The variation with frequency is also satisfactory (fig. 3): the increase for the low tones, desirable for music, is found by no means to give the hall an echoing or „hollow” character. It must still be noted that this frequency characteristic is only valid for the reverberation, which results from repeated reflection at the walls. The contributions of importance for intelligibility reach the audience after a single reflection at walls which absorb only a few per cent. The variation of this with the frequency is therefore unable to influence the sound appreciably.

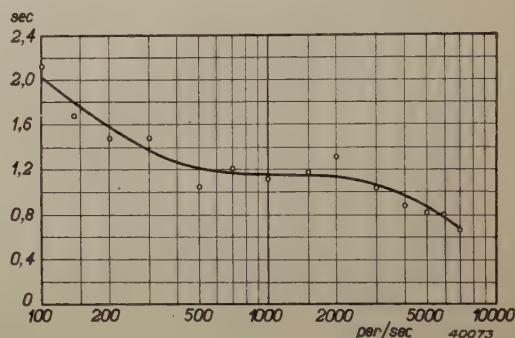


Fig. 3. Reverberation time of the theatre auditorium in Utrecht as a function of the frequency. The reverberation time was measured with the source on the stage, where a normal scene had been set up. The measurement was carried out for each frequency at three points in the auditorium and one on the balcony. The reverberation time at 200-2000 c/s amounts to 1.2 sec. and increases at low frequencies to 1.0 sec for 100 c/s; in the high tones the reverberation time decreases to 0.7 sec. for 7 000 c/s.



## CONSIDERATIONS ON THE TEXTURES OF METALS

by J. F. H. CUSTERS.

62.918

When in a polycrystalline material the crystallographic axis directions of the crystal grains are not entirely at random the material is said to possess a texture. In many practical cases the texture of the material is of great importance. It is our intention to discuss in this periodical a succession of examples in which this is the case. As introduction it is explained in the following article how textures can be represented graphically (stereographic projections of the so-called reference sphere) and how the texture of a given specimen can be determined experimentally by means of X-ray photographs.

It is a well known characteristic of a crystal that its physical and chemical behaviour is in general different in different directions. When for example the tensile strength of a block of copper consisting of a single crystal is measured, it will be found that in the direction of a rib of the cubic crystal lattice it is less than half that measured in the direction of one of the space diagonals of the cubic lattice.

In technology such metals in the form of single crystals only play a subordinate part, because they possess properties which are usually undesired from the technical point of view. The polycrystalline state is of much greater importance, where the metal is built up of a collection of larger or smaller single crystals or crystal grains.

*Fig. 1* shows the surface of a polycrystalline metal as it appears after being etched with a suitable reagent. The various grains can here be distinguished clearly because, after having been

attacked by the reagent, they reflect the light differently. Each of the grains is a single crystal. They are, however, usually not bounded by crystal planes as is often the case with single crystals encountered in nature, which commonly possess a symmetrical external shape; the boundaries in this case are rather determined by the more or less accidental meeting of grains growing from different points, which are later perhaps deformed, due, for instance to mechanical treatment.

It is important to note that each of these grains has its own crystallographic axis direction and that these directions, due to the varied positions of the grains, are in general different from grain to grain as represented schematically in *fig. 2a*. It may, however, also occur that each crystal grain occupies a definite, more or less sharply distinguished, preferred position, as far as the position of its crystal axes is concerned, as represented in *fig. 2b*. In this case the polycrystalline material is said to exhibit a texture. A material thus has a texture as soon as the grains no longer occupy absolutely irregular positions, as is assumed in *fig. 2a*.

The examples of *figs. 2a* and *b*, represent the two extreme cases of orientation: in the first case no texture, in the other case a texture of such a nature and completeness that the material may be said to be a pseudo single crystal. In addition to these limiting cases all types of textures can be found. As an example we may mention the texture of a drawn aluminium wire. When, beginning with a polycrystalline wire with non-orientated crystal positions, the wire is strongly stretched, the particles take up such positions that in each grain a space diagonal of the (cubic) crystal lattice lies in the direction of stretch, while for the rest the orientation still remains random (*fig. 2c*).

In general in a polycrystalline metal the above mentioned dependence on direction of the different properties of a crystal will not be noticed if the crystalline particles are non-oriented. Due to the random position of the particles the crystal properties in each direction of the polycrystalline metal constitute a sort of average over all



*Fig. 1.* Photomicrograph of polished and etched  $\alpha$ -brass (magnified 100 times). The polycrystalline structure is here clearly visible because of the fact that the different crystal grains reflect the light in different ways.



directions; the material thus behaves as an isotrope as long as the observations involve the collaboration of a sufficient number of particles. If on the contrary the material exhibits a texture, it may be expected that a dependence of the properties on direction will be observable. A typical example of this which has already been mentioned in this periodical<sup>1)</sup> is reproduced

following numbers of this periodical. The relation which is found between the texture and other properties of metal will there also be emphasized as far as possible.

### Description of a texture

Let us begin with the methods which are used for describing a texture. We consider a

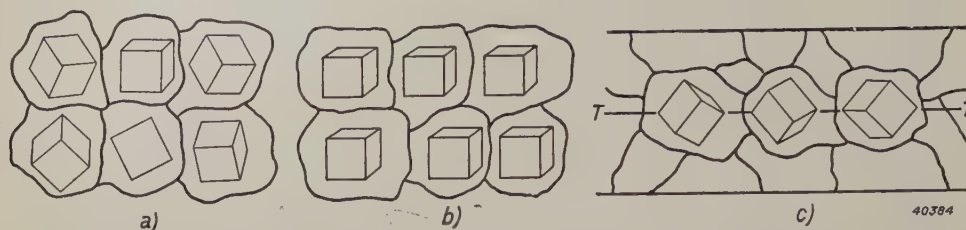


Fig. 2. Position of the crystal axes in the particles of a polycrystalline material with a cubic crystal lattice.

- a) No texture: the particles lie with their axes entirely at random.
- b) Sharp texture: the axes of all the particles are in the same position.
- c) Texture of an aluminium wire drawn in the direction  $TT$ : in each particle a space diagonal of the cubic lattice is parallel to  $TT$ .

ced in *fig. 3*: upon drawing cups of chrome-iron sheet very different results were obtained according to whether or not the original material exhibited a texture.

In judging a material for a given use all kinds of other properties in addition to the texture naturally also play a part. For example, the dimensions of the crystal grains (fine or coarse) may also be of decisive importance. The presence or absence of stresses in the crystal particles may also be important. In general therefore a whole complex of properties should be studied in the case of a metal intended for a given purpose. We shall here, however, direct our attention especially to questions connected with the texture. For that purpose we shall in this article discuss the way in which textures are investigated and described, while it is our intention to discuss a series of examples in the

<sup>1)</sup> W. G. Burgers, Philips techn. Rev. 2, 156, 1937.

polycrystalline piece of metal in which there are hundreds of crystal grains. Let the crystal lattice be of the cubic type. In each single crystal the atoms which occupy the lattice points are arranged in a definite way so that planes can be distinguished which are regularly filled with lattice points. In *fig. 4* several of these planes are indicated. These are the lattice planes at which X-rays can be „reflected” (see below). If we confine our attention to the cube planes (*fig. 4b*), three mutually perpendicular sets may be distinguished. It is obvious that the position of a crystal grain is completely defined when the position of its cube planes is known, while of course the directions of the normals to these planes also fully determine the position of the crystal particles.

Returning to the piece of metal mentioned, a sphere is drawn about it, the so-called reference sphere whose radius is large compared with the

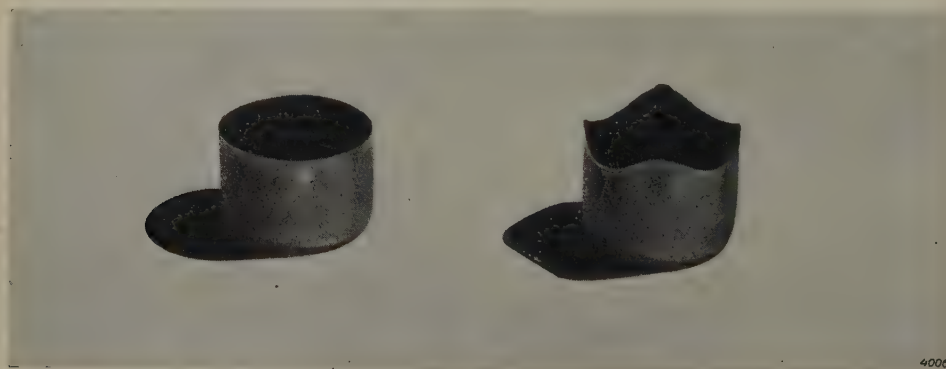


Fig. 3. Cups made of chrome-iron sheet, obtained by drawing. In the case of the left-hand cup the original material had no texture, in the case of the right-hand cup a texture was present.



dimensions of the piece of metal. The position of the three cube planes of each particle is investigated; the three normals to these planes are drawn through the centre of the sphere and extended until they pierce the sphere as shown in *fig. 5* for a single grain<sup>2</sup>). This is done for

bodododecahedron planes<sup>3</sup>) (*fig. 4c*) to describe a texture. In the case of cubic crystals one usually confines oneself to the cube and octahedron planes.

In order to draw and measure a texture easily, it is desirable to represent the reference sphere

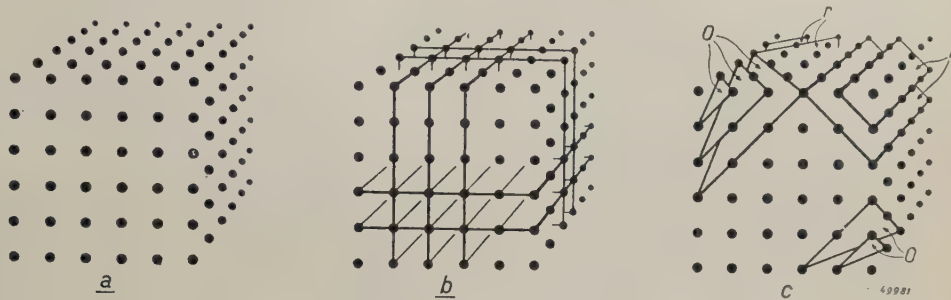


Fig. 4. *a*) Diagrammatic representation of a cubic lattice. *b*) The three sets of cube planes. *c*) Octahedron planes *o* and rhombododecahedron-planes *r*. (After M. Polanyi).

every grain. In this way the surface of the sphere becomes filled with points. The density of the points on the sphere is the same at all points when the piece of metal exhibits no texture. In contrast to this, the density will be different from point to point when the crystal

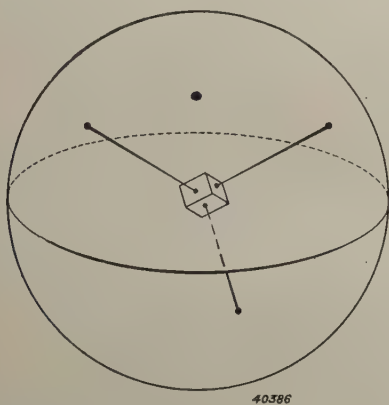


Fig. 5. Reference sphere drawn around a single crystal. The normals to the three cube faces passing through the centre of the sphere are indicated. These normals pierce the surface of the sphere at three points which are called the poles of the cube planes.

grains are more or less oriented. In *fig. 6b* this is shown for the texture of *fig. 2b*: at only three spots, which are more or less extended according to the sharpness of the texture, is the surface of the sphere „blackened”. The texture of the abovementioned aluminium wire (*fig. 2c*) is represented in the same way in *fig. 7b*.

Use may be made not only of the cube planes but also of the so-called octahedron or rhom-

just considered on a plane by means of a projection. The ordinary method is that of stereographic projection, which is explained in *fig. 8*. A plane is drawn through the centre of the reference sphere, the projection plane *Pr*. The normal to this plane through the centre *C* pierces the sphere at the „North” and „South” poles, *N* and *Z*, respectively<sup>4</sup>). Points lying on the surface of the upper hemisphere are now projected upon *Pr* by connecting them with the south pole and finding where the connecting lines cut the plane *Pr* (*S'* is the projection or image of *S*), while the points lying on the lower hemisphere are projected by connecting them with the north pole and marking the points of intersection of them with the north pole and marking the points of intersection of the connecting lines and the plane *Pr* (*T'* is the image of *T*). In this way all the projected points are made to lie within the so-called basic circle *G*. Points on the upper and lower hemispheres can be distinguished in the projection by marking them blue and red, respectively, for example. In practice this will usually be unnecessary because the texture of the material almost always possesses a plane of symmetry; this plane is then chosen as projection plane so that the projections in blue and red then have exactly the same appearance and one of them is sufficient.

<sup>3</sup>) The planes are so called because upon reflection at the different planes of symmetry of the lattice, an octahedron or a rhombododecahedron, respectively, results from one such plane.

<sup>4</sup>) From this nomenclature it is evident that it is here a question of a procedure whose oldest and most important field of application is in geography in representations of the earth.

<sup>2</sup>) Actually two normals are enough to determine the position of the crystal grain, but for the sake of the symmetry all three are always considered.



The pattern which is obtained when the points of intersection on the sphere of the normals corresponding to a given type of lattice plane are projected is called the pole figure for the corresponding plane. From two such pole figures, for example, that for a cube and that for an octahedron plane, a good idea of a texture can be obtained. In fig. 6c and 7c the pole figures are drawn for the cube plane of the two textures of fig. 2b and c.

How is the texture of a given material now determined? The method which is generally used for by this makes use of the diffraction of X-rays by crystals.

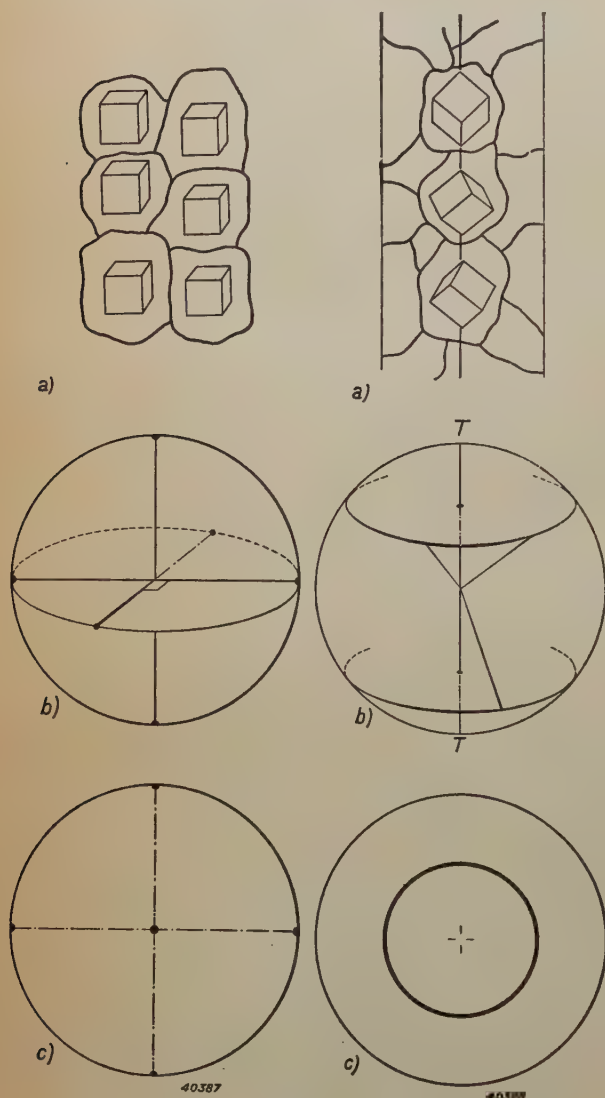


Fig. 6.

Fig. 7.

Fig. 6. The texture of fig. 2b shown again in a) is represented on the reference sphere. The reference sphere is blackened at only three poles (and their three „counter poles”). In c) the projected pole figure is given (see below).

Fig. 7. Like fig. 6, for the texture drawn in fig. 2c. The reference sphere is blackened in two circles (parallel and counter parallel circle); they indicate the geometrical position of the points of intersection of the normals to the three cube planes in each particle.

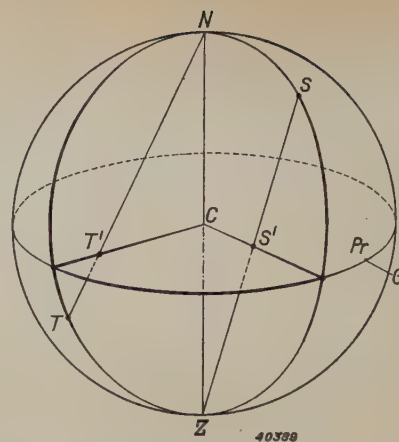


Fig. 8. Stereographic projection on the plane *Pr* of points lying on the reference sphere. *S* is the image of *S*, *T'* that of *T*.

### X-ray determination of a texture

When X-rays of a given wave length  $\lambda$  (monochromatic radiation) fall upon a crystal, no diffraction will in general be observed, since the rays refracted at the lattice points cancel each other by interference. Only when Bragg's condition:

$$n \lambda = 2 d \sin \Theta,$$

is satisfied, does the interference of the rays deflected in certain directions lead, not to cancellation, but to mutual reinforcement. In this equation  $d$  is the distance between some set or other of parallel lattice planes.  $\Theta$  the angle at which the beam of X-rays strikes the lattice plane (thus  $90^\circ - \Theta$  is the angle between the beam and the normal to the plane), and  $n$  is a whole number. The direction in which the deflected rays reinforce each other and which can therefore be determined experimentally, can now be described for a given lattice plane as if the X-rays were reflected against that lattice plane as against a mirror. With given values of  $d$  and  $\lambda$  this reflection, according to Bragg's condition, can occur at various angles of incidence  $\Theta$  which correspond to the values  $n = 1, 2, 3, \dots$ . One then speaks of reflections of the 1st, 2nd, 3rd ... order. (The physical significance of  $n$  is then the number of wave lengths difference in path between X-rays which are reflected by successive lattice planes).

Example: with the help of an X-ray tube with copper anode, using suitable filters, a strong, practically monochromatic X-radiation can be obtained with the wave length  $\lambda = 1.539 \text{ \AA}$  (Cu  $K\alpha$  radiation). If this beam is allowed to fall upon a crystal of aluminium of which a first order reflection of the octahedron plane is desired (the lattice plane distance is  $d = 2.333 \text{ \AA}$  in this case), the beam of X-rays must strike that plane at an angle of  $19^\circ 16'$ .

In fig. 9 let  $V$  be the representative of some set of mutually parallel lattice planes in a



crystal grain.  $V$  is assumed to be in such a position relative to the incident X-ray beam that Bragg's condition is satisfied. Then the normal  $n$  to  $V$  includes an angle  $90^\circ - \Theta$  with  $S$ . It is clear that at every position of  $V$  in which  $n$  lies on the surface of the cone indicated in fig. 9 (apex  $O$ , axis  $S$ , semi-apex angle  $90^\circ - \Theta$ ), reflection of the X-ray beam will occur. We now draw a sphere around  $O$  as a centre which can be used as the above described reference sphere. The cone mentioned cuts the sphere along the so-called reflection circle  $R$ , and on this circle therefore the point of intersection (pole) of the normal to the surface  $V$  must always lie if that surface is to cause a reflection of a given order of the X-ray beam  $S$ . In fig

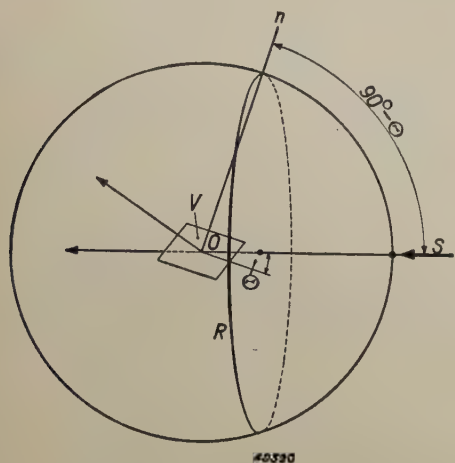


Fig. 9. A beam of X-rays  $S$  is reflected at a lattice plane  $V$  of a crystal only when the angle between  $S$  and the normal  $n$  to  $V$  is equal to  $90^\circ - \Theta$  (Bragg's condition). Therefore for each position of  $V$  in which  $n$  lies on the surface of a cone with the semi-apex angle  $90^\circ - \Theta$  will there be reflexion. The surface of this cone cuts the reference sphere drawn around the crystal in a circle, the so-called reflection circle  $R$ . In the case of reflection, therefore, the pole of the lattice plane in question must lie on this circle.

10 three positions of  $V$  are assumed which satisfy this condition (points of intersection  $N_1, N_2, N_3$ ).

Let us now consider the reflected radiation. In the case of fig. 10 it will cause three spots ( $P_1, P_2, P_3$ ) on a photographic film  $F$  placed behind the crystal; these spots may be considered as the „images” of the positions  $V_1, V_2, V_3$  of the lattice plane. It is clear that the angles  $\alpha_1, \alpha_2, \alpha_3$ , which the projections (on a plane perpendicular to  $S$ ) of the normals  $n_1, n_2, n_3$  inclose, are the same as the corresponding angles between  $P_1, P_2, P_3$  on  $F$ ; in other words in this projection the angles are retained.

At the point  $O$  we now place a fragment of polycrystalline metal with a cubic lattice, and we again consider a single type of lattice plane of the single crystal grains, for instance the

cube planes. In the absence of a texture in the fragment the reference sphere will be uniformly covered with the poles of those planes, with the result that a complete circle of „images” is

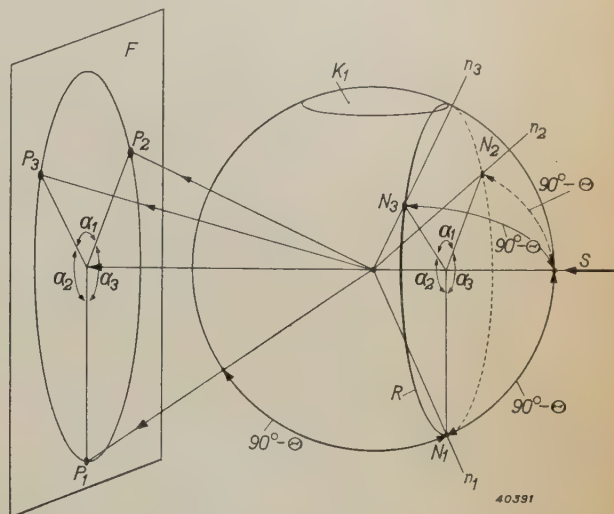


Fig. 10. The points  $P_1, P_2, P_3$  on the photographic film  $F$  are the images of three positions of the lattice plane at which reflection takes place. The normals  $n_1, n_2, n_3$  to the lattice plane in the three positions pierce the reference sphere at the poles  $N_1, N_2, N_3$ . From this it is easily deduced that the „blackened” parts of the reflection circle  $R$  are projected on  $F$  in such a way that the angles ( $\alpha_1, \alpha_2, \alpha_3$ ) are retained.

formed, a so-called Debye-Scherrer ring, whose radius is determined not only by the wave length  $\lambda$  and the distance between the lattice planes  $d$  but also by the distance at which the film is situated from the crystal fragment. In fig. 11 an X-ray photograph may be seen with a number of such quite uniformly blackened circles. If on the contrary the crystal fragment does possess a texture, so that only certain parts of the reference sphere are „blackened”, then in general the Debye-Scherrer

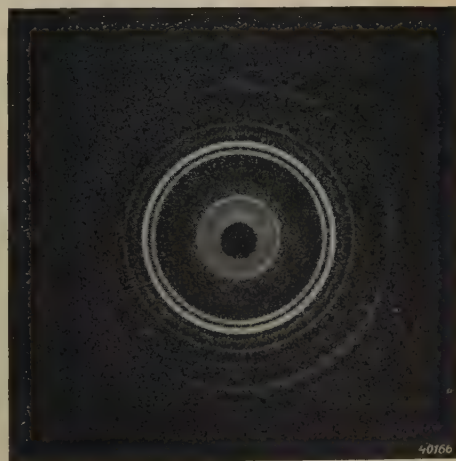


Fig. 11. X-ray photograph of a substance in powder form which naturally possesses no texture and therefore gives entirely uniformly blackened Debye-Scherrer rings.



ring on the film is not uniformly blackened, but only those segments of it which are the image of the parts of the reflection circle where this circle passes through „blackened” regions on the reference sphere.

When one has thus obtained such an X-ray diffraction photograph of a piece of metal, then by measuring the angles within which a given Debye-Scherrer ring is blackened it can immediately be found along what part of the corresponding reflection circle  $R$  a blackening must be present on the reference sphere. The reflection circle, however, covers only a small part of the reference sphere, while for judging the texture we must know the blackening over the whole reference sphere (unless this requirement may in part be neglected because of

symmetry properties of the texture). One of the means of ascertaining this would be to choose a succession of different wave lengths of the X-ray beam, so that the reflection circle  $E$  moves parallel to itself over the reference sphere and the whole reference sphere is as it were scanned. In practice, however, this method encounters insuperable difficulties, the chief among which is the fact that one cannot have at one's disposal a set of X-ray tubes each of which furnishes radiation of a different wave length. The more obvious and commonly employed method of scanning the reference sphere is usually to give the crystal fragment in question a slightly different position each time. If the reference sphere is assumed to be rigidly connected with the crystal, while the positions

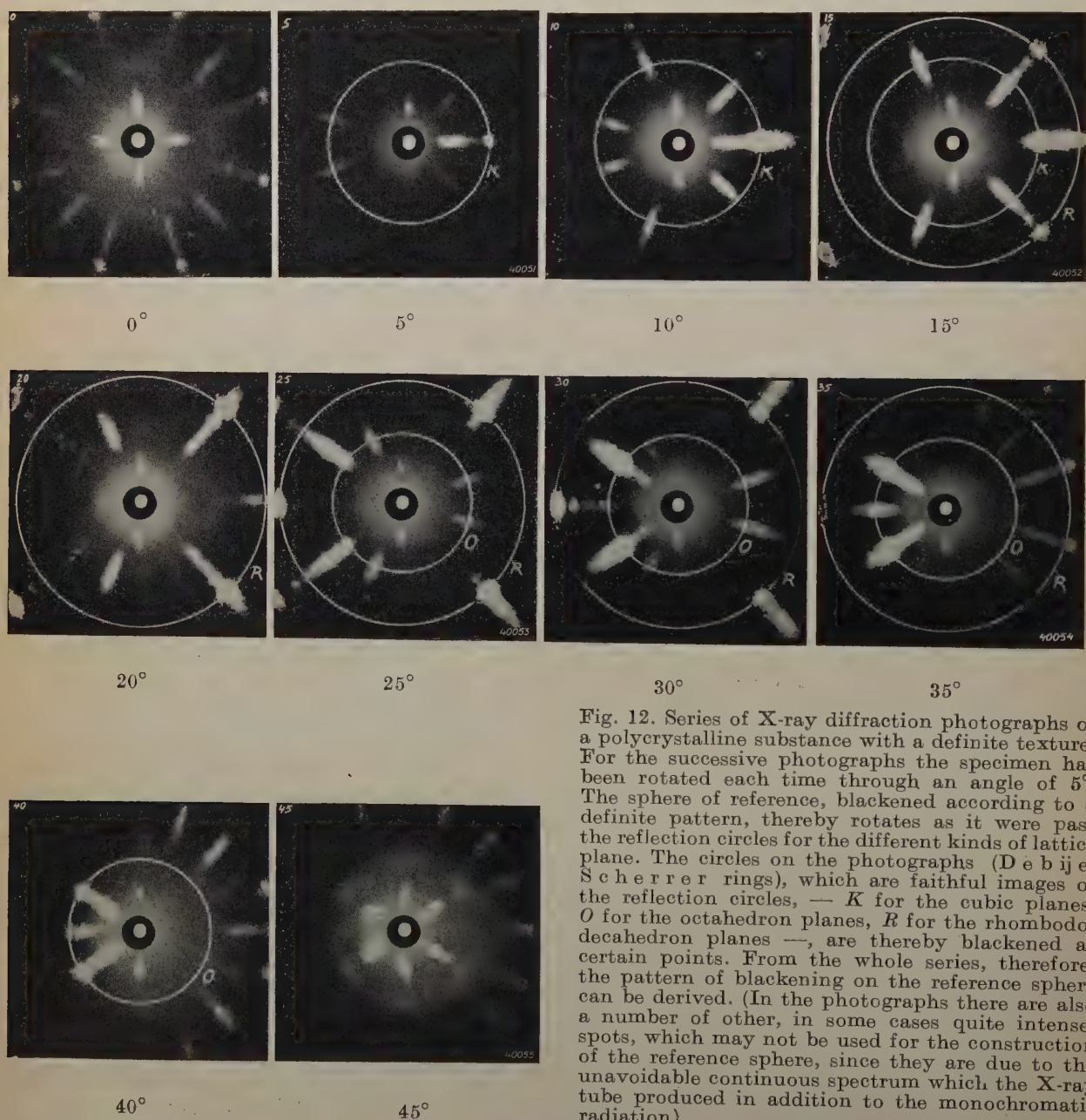


Fig. 12. Series of X-ray diffraction photographs of a polycrystalline substance with a definite texture. For the successive photographs the specimen has been rotated each time through an angle of  $5^\circ$ . The sphere of reference, blackened according to a definite pattern, thereby rotates as it were past the reflection circles for the different kinds of lattice plane. The circles on the photographs (Debye-Scherrer rings), which are faithful images of the reflection circles, —  $K$  for the cubic planes,  $O$  for the octahedron planes,  $R$  for the rhombodecahedron planes —, are thereby blackened at certain points. From the whole series, therefore, the pattern of blackening on the reference sphere can be derived. (In the photographs there are also a number of other, in some cases quite intense, spots, which may not be used for the construction of the reference sphere, since they are due to the unavoidable continuous spectrum which the X-ray tube produced in addition to the monochromatic radiation).



of  $S$ ,  $R$  and  $F$  are constant, different parts of the sphere turn with the crystal past the reflection circle  $R$ . The crystal fragment (for instance a piece of rolled strip or the like) is usually rotated through a certain angle,  $5^\circ$ , for example, from a given initial position about a vertical axis passing through the centre of the sphere, and in each position a photograph is taken. In *fig. 12* is shown a series of photographs taken in this way of a certain material. By this method of procedure the whole reference sphere is scanned with the exception of caps at the top and bottom,  $K_1$ ,  $K_2$  (in *fig. 10* the cap  $K_1$  is indicated). In order to include these caps also the fragment is rotated about a different axis, for instance about the line perpendicular to the plane of the drawing.

### The construction of the pole figure

In the manner described the blackening pattern on the reference sphere of the fragment investigated can be constructed for the lattice plane considered, for example the cube plane. Actually, however, as explained above, we desire to obtain a plane pole figure by projecting the reference sphere on a plane passing through its centre. As plane of projection it is preferable to choose a plane of symmetry of the object in question (at least if the object possesses such a plane), since it may be expected that this will also be a plane of symmetry of the texture. Beginning with the X-ray photographs the pole figure can now also be drawn immediately on

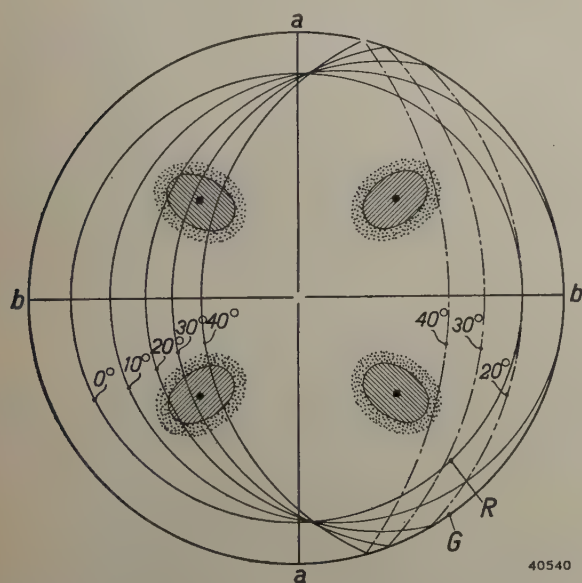


Fig. 13. Pole figure for the cube plane derived from the photographs in *fig. 12*. The projection of the reflection circle is indicated for a number of rotated positions of the piece of metal. It may be seen that at about  $10^\circ$ , it passes through the middle of the blackened region at the right-hand end of the axis  $b-b$ . In the photographs at  $10^\circ$  and  $15^\circ$  of *fig. 12* the ring  $K$  exhibits an intense blackening at the corresponding point.

this plane, without first following the circuitous method *via* the reference sphere. For this purpose on the projection plane for each photograph the projection is drawn of the reflection circle which corresponds to the Debye-Scherrer ring considered, and only those

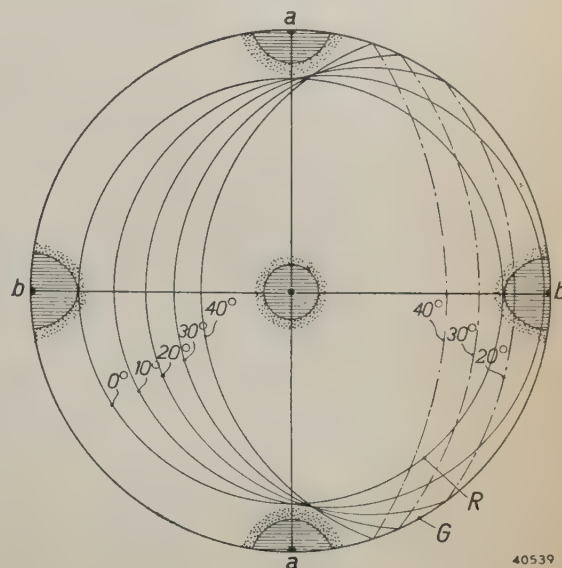


Fig. 14. Pole figure for the octahedron plane derived from the photographs of *fig. 12*. In the positions  $30^\circ$  to  $40^\circ$  the reflection circle passes through blackened regions which can be recognized in *fig. 12* in the corresponding photographs as blackening of the corresponding segments of the ring  $O$ .

segments of the projected circle are „blackened” which can be recognized as blackened segments of circles of the Debye-Scherrer ring on the film. It must be kept in mind that only in one position of the object (for instance, the initial position) is the plane of symmetry, which has been chosen as plane of projection, and which is bound to the object, parallel to the plane of the reflection circle which is bound to the incident X-rays (namely perpendicular to their direction). Thus in working out the diffraction photographs taken in rotated positions of the object, one must project the successive reflection circles provided with the appropriate blackenings in each case on the projection plane which has rotated farther with the object. This apparently difficult operation is carried out in practice easily and quickly by means of a so-called Wulff net. We shall not go unnecessarily deep into the details here, however.

In this way, for every desired lattice plane of the object, the pole figure can be constructed by considering the Debye-Scherrer ring corresponding to that lattice plane. In *fig. 13* and *14* we show the pole figures thus obtained, which are derived from the series of photographs of *fig. 12* for the cube plane and for the octahedron plane, respectively.



# THE MEASUREMENT OF PEAK VOLTAGES IN A STUDIO INSTALLATION

by F. de FREMERY and J. W. G. WENKE. 621.317.726 : 621.396.712.3

A measuring apparatus is described which is used in a broadcasting studio for a continuous control of the alternating voltages which are sent to the transmitter. In connection with the purity of the broadcast these voltages must not exceed certain limits. Since there is a danger of their doing so, particularly at the peaks of the recorded sound, special provision has been made for convenient reading off of the peak voltages by means of a retardation arrangement.

The amplitudes of the alternating voltages which are generated in the electrical transmission of sound vibrations must lie between two limits: the voltages must on the one hand project far enough above the level of interferences (noise), and on the other hand the amplitude must not become so great that a disturbing non-linear deformation occurs in one of the links of the transmission.

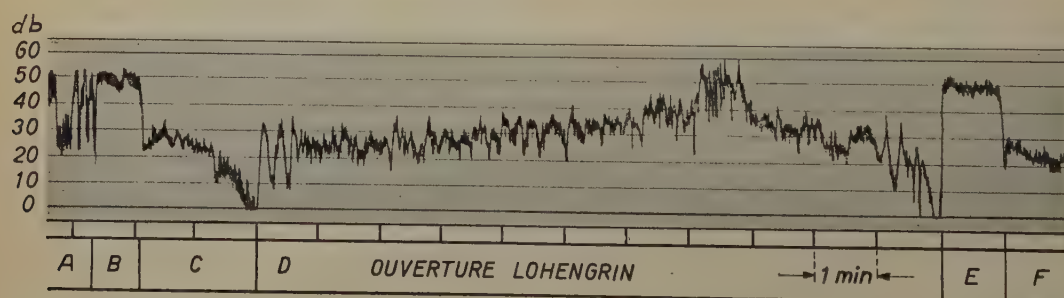
An especially important part is played by these two conditions in the running of a broadcasting studio. In this case the aim is to secure the greatest possible freedom from interference and purity of reproduction, while the amplitude of the sound vibrations, at least when it is a question of music, exhibits great variations. It is in just these variations that the dynamic quality of the music lies. As an illustration a registrogram of the sound intensity in a concert hall during the performance of a piece of music is reproduced in *fig. 1*. In order to provide that the alternating currents which are sent from the studio to the transmitter are sufficiently free of distortion even at the peaks of sound, it will often be necessary to reduce the peaks artificially by decreasing in a suitable way and at the correct moment the amplification which is applied to the microphone voltages. On the other hand in the soft passages of the music it will be desirable to increase the amplification somewhat in order that the reception of those passages may suffer as little as possible from interferences. The regulation of the correct de-

grees of amplification for each part of a piece of music is the task of the technician who, seated at a control table, supervises and controls the whole broadcast.

In order to carry out this regulation the technician must know in advance the moments at which peaks may be expected as well as their intensity. In this he is aided by the score which lies before him and the experience gained at the rehearsals which precede the actual broadcast. In addition, however, the technician must have some method of checking whether the regulation he performs is having the desired effect. The desired check is obtained not only by means of a loud speaker which is connected with the line to the transmitter and with which it is possible to determine subjectively whether or not distortion occurs, but also by means of a measuring instrument which indicates continuously the amplitude of the alternating voltage on the line to the transmitter.

The principle of the measuring instrument which was used for this purpose in a studio installation previously described in this periodical<sup>1)</sup> is shown in *fig. 2*. It contains two amplifier stages in push-pull connection, followed by a rectifier and an output amplifier stage. The anode current of the final stage, which is a measure of the amplitude of the input A.C. voltage of the apparatus, is measured with a moving coil instrument with a light pointer

<sup>1)</sup> F. de Fremery and J. W. G. Wenke, Philips techn. Rev. 6, 139, 1941.



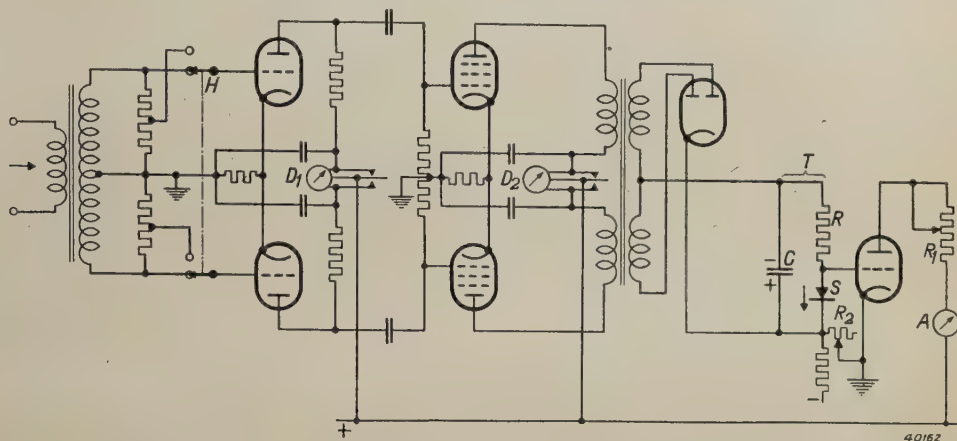
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Fig. 1. Variation of the sound intensity in a concert hall during the performance of a piece of music: Overture to Lohengrin. (From: R. Vermeulen, The relationship between fortissimo and pianissimo, Philips techn. Rev. 2, 266, 1937).



which is built into the control table, see *fig. 3*. In series with this instrument a second meter is connected, which, together with the actual amplifier connection, is assembled on a panel of the amplifier racks of the studio installation, so that the broadcast can be controlled there also. The scale of the instrument is calibrated in decibels and runs from  $-45$  to  $+45$  dB. The value  $0$  dB thereby corresponds to an input

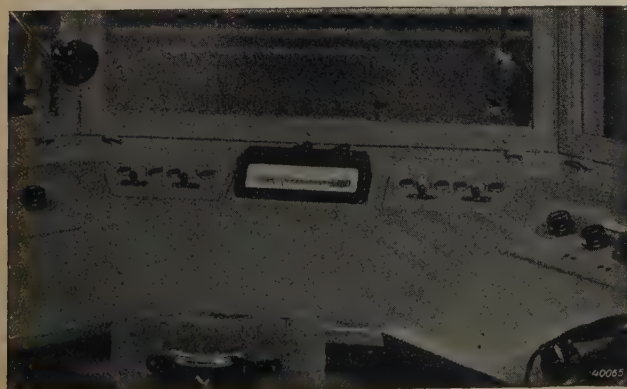
reason a device has been employed which very much facilitates the reading off of voltage peaks in particular, with which we are chiefly concerned. The rectified signal voltage is not fed to the output amplifier valve directly, but *via* the time circuit indicated by *T* in *fig. 2*. This consists of a connection in parallel of a condenser *C* and a potentiometer, the latter being composed of a resistance *R* and a high



*Fig. 2.* Connections of the peak voltage meter. *T* time circuit consisting of a condenser *C* and two resistances *R* and *S*. For reasons explained below the leakage resistance of a blocking-layer rectifier is used for *S*. A ammeter calibrated directly in dB of the input signal. *D*<sub>1</sub> and *D*<sub>2</sub> differential ammeters.

A.C. voltage of  $1.55$  VR.M.S., which is considered as the normal, permissible zero level in broadcasting transmissions over lines with an impedance of  $200$  ohms (transmission power  $12$  mW). The part of the scale above  $0$  dB is coloured red as an indication that the A.C. voltages here exceed the prescribed limit and that there is therefore danger of distortion.

Upon rapid alternation of the amplitude of the input voltage it would be very fatiguing for the person at the control table to follow the light spot on the scale of the indicator as it continually jumps back and forth. For this



*Fig. 3.* Indicating instrument of the peak voltage meter built into the control table of the broadcasting studio.

resistance *S*, which we shall discuss later. If an A.C. voltage of constant amplitude is now fed to the input of the connections, the condenser *C* is charged to a certain voltage and a very small current flows through *R* and *S*. The grid of the output amplifier valve thereby assumes a certain negative voltage. If the amplitude of the input A.C. voltage increases, the condenser *C* is very quickly charged to a higher voltage and simultaneously the grid of the output valve becomes more negative, whereupon the indication of the anode current meter immediately adjusts itself to the new value. If, however, the amplitude of the input A.C. voltage now becomes smaller again, the condenser *C* can only adjust itself slowly, by discharge over *S* and *R*, to the new, lower voltage value, so that the light pointer of the anode current meter moves back only slowly. In this way provision has been made that upon the occurrence of a voltage peak the indicator reaches practically its final value (maximum deviation  $1$  dB) within  $0.005$  sec, while it falls back at a rate of only about  $20$  dB per second.

The relation between the anode current of the output stage and the input A.C. voltage, *i.e.* the calibration of the scale of the indicator, depends in the first instance on the characteristics of the amplifier valves used, in particular on that of the output valve. Since with increa-



sing input A.C. voltage to the whole circuit the grid of the output valve becomes more strongly negative, with increasing input A.C. voltage the anode current will decrease. Due to the curvature of the  $i_a-v_g$ -characteristic the variation in anode current thereby becomes smaller and smaller just in the region of high input A.C. voltages in which we are especially interested, so that there as it were the scale is compressed. In order to avoid this undesired effect, a normal resistance is not used for the resistance  $S$  of the potentiometer in fig. 2, but one which is dependent on voltage, namely the

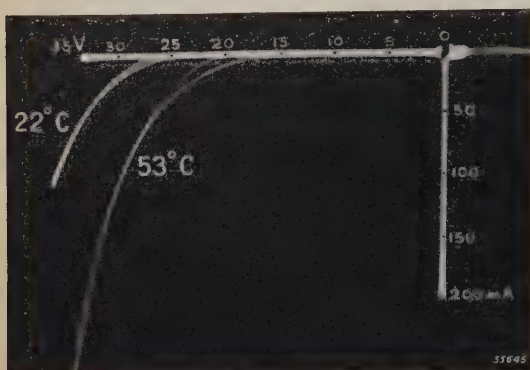


Fig. 4. Relation between leakage current and blocking voltage (blocking characteristic) of a selenium valve, at two different temperatures. (From: D. M. D u i n k e r. The use of selenium valves in rectifiers, Philips techn. Rev. 5, 199, 1940).

leakage resistance of a blocking-layer rectifier (selenium valve). In fig. 4, where the blocking characteristic of such a valve is given it may be seen that the very high resistance of the valve in the blocking direction (leakage resistance) decreases with increasing voltage and changes correspondingly the voltage division through the potentiometer  $R$ - $S$  in such a way that with increasing input A.C. voltage the negative grid voltage of the output valve increases less than proportionally. By giving  $S$  and  $R$  suitable dimensions a fairly linear dB scale could be obtained for the indicating instrument.

Upon changing valves, etc. the calibration of the scale is checked in two steps: an A.C. voltage of 1.55 V R.M.S. is applied to the input terminals, and by adjusting the regulatory resistance  $R_2$ , which affects the grid bias voltage of the output valve, the pointer of the dB-meter on the amplifier rack is set exactly at 0 dB. In order to fix a second point on the scale, by reversing the switch  $H$ , the grid A.C. voltage of the first set of amplifier valves is then reduced by a factor which corresponds to an attenuation of the input signal by 30 dB. By adjustment of the resistance  $R_1$  the indication of the anode current meter is then set at -30 dB. Since

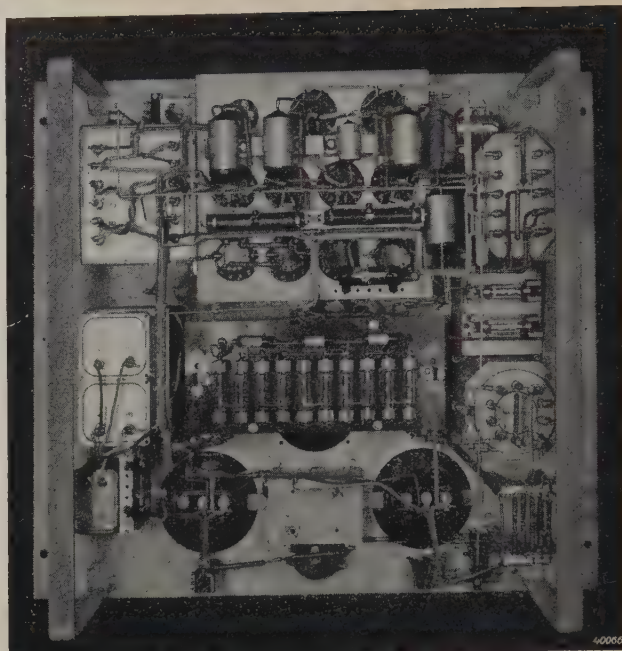


Fig. 5. The peak voltage meter opened. At the top centre is a panel for all the amplifier valves with their grid resistances, decoupling condensers, etc. Below it the potentiometer of the time circuit. The blocking-layer rectifier in this part is composed of three selenium valves connected in parallel. The potentiometer is covered with a double-walled metal cap.

only a small anode current flows at a high input A.C. voltage (0 dB), so that the adjustment of  $R_1$  has little effect, the first calibration point remains practically unaffected in the fixing of the second.

Fig. 4 shows that the blocking characteristic of the selenium valve still depends very much upon the temperature. This dependence can be

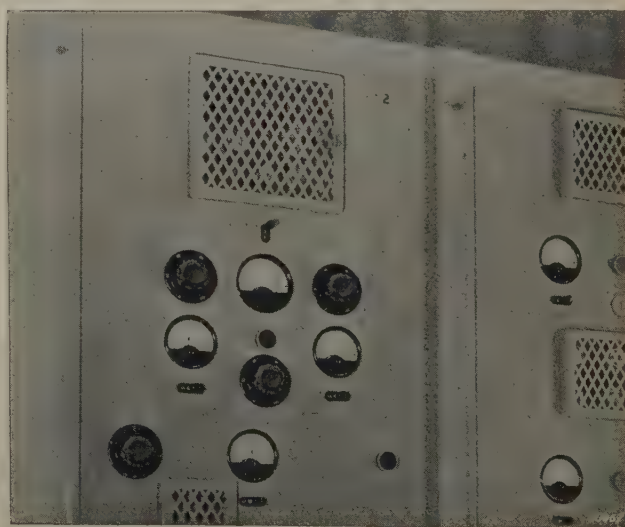


Fig. 6. Front view of the peak voltage meter mounted in an amplifier rack. The dB-meter is in the middle and below it the two differential meters with the corresponding keys. The amplifier valves are accessible through the door above.



expressed by a temperature coefficient of the leakage resistance, which coefficient is found to be approximately independent of the voltage in the voltage region in question. It is thus possible to make the calibration of the instrument independent of the temperature by making the resistance  $R$  of a material whose specific resistance has the same temperature coefficient as the leakage resistance of the valve. When that is done the voltage division through the potentiometer remains unchanged upon variations in the temperature. Care must now of course be taken that the resistance  $R$  and the valve are always at the same temperature, but this is easily ensured by housing them both in a double-walled heavy metal box, which because of its large heat capacity makes it possible for temperature fluctuations of the surroundings to in-

fluence only the temperature inside the box and not the temperature distribution. In *fig. 5*, in which the peak voltage meter is shown open, this box has been removed in order to show the parts of the potentiometer.

The influence of mains voltage fluctuations on the calibration is also eliminated by stabilizing with neon lamps the plate voltage which is provided by the supply apparatus. Moreover, the plate voltage of the first two amplifier stages can be checked with two meters. These are differential meters (see *fig. 2*) which in normal use indicate the difference in current between the two valves in push-pull connection of each stage. By reversing keys which are situated under the meters, see the photograph *fig. 6* of the complete apparatus, the plate current of each valve can, however, be measured separately.

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# A $pH$ -METER WITH A VERY HIGH INPUT RESISTANCE

by C. DORSMAN.

545.37 : 621.317.723

In very many chemical processes the degree of acidity is an important factor. This is expressed by the quantity  $pH$ , defined as the negative Briggsian logarithm of the concentration of the hydrogen ion. In this article a discussion is given of several electrical methods, based upon Nernst's law of measuring the  $pH$ . The  $pH$ -meter manufactured by Philips is described; it contains an electrometer with compensator as well as complete chemical apparatus. The electrometer differs from existing instruments in that the D.C. voltage to be measured is converted into an A.C. voltage. This has the advantage that the input resistance is very high, since it is determined only by the resistance of two condensers with air as dielectric. Because of this high input resistance the instrument is particularly well adapted to measurements with the glass electrode. At the same time, an amplifier for A.C. voltage can be made stabler than one for D.C. voltage.

During the last twenty years the importance of an accurate knowledge of the degree of acidity of the most diverse liquids has come to be more and more commonly recognized. Not only in purely scientific research, but also in the chemical industry, in that of food products, in soil chemistry, in laundries and in all kinds of physiological work, the measurement of hydrogen ion concentrations now belongs to the standard methods daily applied in innumerable laboratories.

The concentration of the hydrogen ions varies between about 1 gram-ion per litre in strongly dissociated acids at a concentration of 1 normal, to  $10^{-14}$  gram ion per litre for alkalis of 1 normal. These figures are inconvenient to use. For that reason Sørensen in 1909 proposed the introduction of the negative Briggsian logarithm of the hydrogen ion concentration, expressed in gram ions per litre, as a measure of the  $pH$ . An advantage of the quantity  $pH$  is that the potentials of the electrodes which are used to measure the degree of acidity of liquids are in a linear relation to it. This is expressed in Nernst's law which we shall now discuss.

## Nernst's law

The relation between the difference  $\Delta E$  in voltage between two solutions separated by a semi-permeable wall and the concentrations  $C_1$  and  $C_2$  in which a certain kind of ion which can pass through this wall is present in the two solutions (fig. 1) is given by the following formula:

$$\Delta E = \frac{RT}{F} \ln \frac{C_1}{C_2}, \quad (1)$$

which among other things describes the equilibrium of the hydrogen ions at a glass electrode. In this equation  $R$  represents the gas constant,  $F$  the charge per gram molecule,  $T$  the absolute temperature.

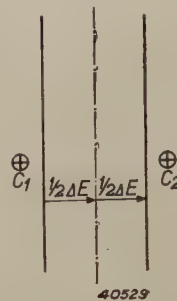


Fig. 1. A semipermeable wall separates two liquids in which an ion occurs with the concentrations  $C_1$  and  $C_2$ , respectively. Only this ion can pass through the wall. There is a potential difference  $\Delta E$  between the two liquids.

We shall give a brief derivation of formula (1). If the wall is permeable for a certain kind of ion and not for another, a number  $N_1$  per second will pass from left to right, which number is determined by the concentration  $C_1$ . At the same time a number  $N_2$ , determined by  $C_2$  will pass from right to left. Due to a potential difference  $\Delta E$  between the two solutions the positive ions will show a preference for one direction. According to the well-known probability relation, the chance that a monovalent ion which strikes the wall will reach the middle plane of the wall from the left is:

$$e^{-q \frac{\varphi - \frac{1}{2} \Delta E}{kT}} \quad \text{and from the right:} \quad e^{-q \frac{\varphi + \frac{1}{2} \Delta E}{kT}}.$$

In these expressions  $e$  is the base of the natural logarithms,  $a$  a potential difference which determines the probability of reaching the middle when there is no external potential difference  $\Delta E$  present.  $k$  is Boltzmann's constant and  $q$  is the charge of the electron. The total number of ions which passes from the left to the middle of the wall is proportional to this factor times the number of ions, which number is proportional to the concentration  $C$ , so that

$$N_1 \sim C_1 e^{-q \frac{\varphi - \frac{1}{2} \Delta E}{kT}} \quad \text{and} \quad N_2 \sim C_2 e^{-q \frac{\varphi + \frac{1}{2} \Delta E}{kT}}.$$

The difference in potential  $\Delta E$  at which the same number of particles reach the middle of the wall from the left as from the right may be found from the condition  $N_1 = N_2$ :

$$C_1 e^{-q \frac{\varphi - \frac{1}{2} \Delta E}{kT}} = C_2 e^{-q \frac{\varphi + \frac{1}{2} \Delta E}{kT}},$$

so that:

$$\frac{C_1}{C_2} = e^{\frac{q \Delta E}{kT}}.$$



The difference in potential thus becomes

$$\Delta E = \frac{kT}{q} \ln \frac{C_1}{C_2}.$$

By multiplying numerator and denominator by the number of particles  $N$  in a gram molecule, formula (1) is obtained.

Entirely analogous to this equilibrium, a formula can be derived which describes the equilibrium state at an electrode in a liquid which contains the same kind of ion as the electrode can take up. This is the case for instance with the hydrogen electrode. Ions from the liquid are deposited on the electrode; ions of the same sort are freed from the electrode. The potential difference at which as many are deposited as are liberated is given for monovalent ions by Nernst's law:

$$\Delta E = \frac{RT}{F} \ln \frac{C_1}{K}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which  $K$  is a quantity with the dimensions of a concentration specific for the electrode. We shall make repeated use of this form of Nernst's equation. For  $n$ -valent ions it is only necessary to add a factor  $n$  to the denominator.

#### Methods of measuring the quantity $pH$

The colorimetric method was often used in the past. This is based upon the change in colour of certain, usually organic, indicator substances when the degree of acidity of the liquid changes between certain critical limits. As examples we may mention phenolphthalein which is colourless at  $pH = 8$  and red at  $pH = 10$ , and methyl orange which is red at  $pH = 3$  and yellow at  $pH = 4$ . In such colorimetric measurements it is possible to determine the  $pH$  accurately within one tenth of a unit.

In addition there exist a number of electrical methods of measurement which are based upon Nernst's law and which we shall now discuss briefly in turn.

#### *Measurements with the hydrogen and the quinhydrone electrode*

The so-called hydrogen electrode is an electrode whose surface is covered with atomic hydrogen. It can be prepared by allowing gaseous hydrogen to bubble along a platinum wire covered with platinum sponge. When the electrode is immersed in a fluid containing hydrogen ions, an exchange of ions between liquid and electrode will take place on the platinum sponge as a catalyst. No current flows if the following holds:

$$\Delta E = \frac{RT}{F} \ln \frac{C_H}{K}.$$

The value of the  $pH$  is now determined by measuring the difference of potential  $\Delta E$ . Since the  $pH$  is the negative Briggsian logarithm of  $C_H$  the following is true:

$$\Delta E = -2.30 \frac{RT}{F} pH - 2.30 \frac{RT}{F} \lg K,$$

$$\text{or } \Delta E = E_0 - pH [58.1 + 0.2 (t-20)] \quad . \quad . \quad (3)$$

Here  $E_0 = -2.30 \frac{RT}{F} \log K$  and  $t$  is the temperature in centigrade degrees.

In the case of the so-called quinhydrone electrode an atmosphere of hydrogen around a platinum electrode is also used. For the sake of brevity we shall not go into it more deeply.

#### *Measurements with the glass electrode*

In measurements with the glass electrode a liquid of unknown  $pH$  is separated by a glass wall, which transmits hydrogen ions but no others, from a liquid with a known  $pH$ . An exceptionally suitable kind of glass for this purpose is the Corning glass 015, which consists of 72 per cent of  $\text{SiO}_2$ , 22 per cent of  $\text{Na}_2\text{O}$  and 6 per cent of  $\text{CaO}$  and contains extremely few impurities. Here again no current flows when the potential difference  $\Delta E$  between the two liquids is equal to;

$$\Delta E = 2.30 \frac{RT}{F} (pH_1 - pH_2) \quad \text{or}$$

$$\Delta E = (pH_1 - pH_2) [58.1 + 0.2 (t-20)].$$

This formula holds for the kind of glass mentioned with very slight deviations between the values  $pH = 0$  and  $pH = 9$ .

We assumed that the wall transmits only hydrogen ions and no others, so that we could immediately apply formula (1) to it. If, however, it also transmits other ions, an equilibrium must also be established for them in the same way. Fortunately, however, Corning glass 015 is impermeable to almost all other ions. Only when ions of alkali and alkaline earth metals are present does a so-called salt error occur, which has been quantitatively determined by Dole<sup>1)</sup> for Li, Na, K and Ba. In the case of strongly basic liquids whose  $pH$  is greater than 9, this must be taken into account. It is understandable that this error occurs exactly in the basic region, since there the number of hydrogen ions available for transport of electricity is very small, and therefore a number of other ions will be able to play a relatively more important part.

#### *Comparison electrode*

In the electrical determination of the degree of acidity the potential difference between the unknown liquid and platinum must be measured, or that between the unknown liquid and the liquid with the known  $pH$ . In order to do this

<sup>1)</sup> M. Dole, The theory of the glass electrode, J. Amer. Chem. Soc. 53, 4260, 1931.



a second electrode, the so-called comparison electrode, must be immersed in the unknown liquid. This electrode must form a well defined, unvarying transition from the liquid to the electrical connection wire.

In the apparatus here described a saturated calomel electrode is used for that purpose (fig. 2). For the measurements with

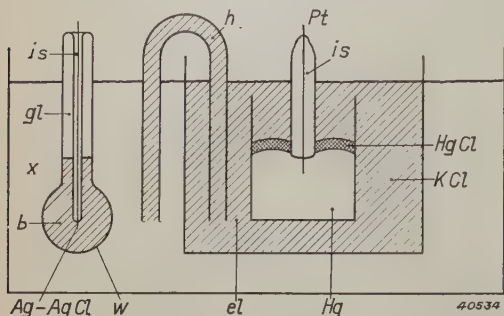


Fig. 2. In the liquid for which the quantity  $pH$  is to be measured a glass electrode ( $gl$ ) and a comparison electrode ( $el$ ) are immersed. The glass electrode, formed by a wall ( $w$ ) which is permeable only for hydrogen ions, is filled with a buffer solution ( $b$ ) with a very constant  $pH$  value. This liquid makes contact with a silver wire covered with silver chloride ( $Ag-AgCl$ ). The latter is insulated by a glass covering ( $is$ ) and is led out at the top through the fused glass. The comparison electrode is filled with saturated  $KCl$  solution ( $KCl$ ), which is connected with the liquid to be measured by a siphon ( $h$ ). The  $KCl$  solution is in contact with the mercury ( $Hg$ ) via a layer of calomel ( $HgCl$ ) covering the mercury. The platinum wire ( $Pt$ ), again insulated with glass ( $is$ ) forms the second connection.

this electrode formula (3) is again valid, taking for  $E_0$  the following values:

+159 upon use of the glass electrode  
 -249.5 " " " " hydrogen electrode  
 and  
 +453.4 " " " " quinhydrone electrode

The method by which this potential difference  $E$  can be measured will now be discussed.

### Methods of measuring the potential difference

The following requirements are made of the method of measurement by the chemist:

- 1) It must be possible to measure with a glass electrode. In practice it is important that this electrode should be sturdy and thus blown from glass several millimetres thick. Then, however, the electrical resistance for current conduction is very high, namely of the order of magnitude of 100 million ohms.

From fig. 3 it may be seen that upon direct measurement of potential a measuring error will occur if the resistance  $R_i$  of the measuring instrument is comparable in magnitude to the glass resistance  $R_g$ . Therefore the requirement is made that the resistance

$R_i$  should be for instance one thousand times as high. It would thus have to be 100000 million ohms.

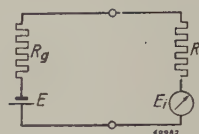


Fig. 3. An instrument with an internal resistance  $R_i$  measures the voltage  $E$  of an electrode circuit whose resistance, determined by the glass electrode is  $R_g$ . The voltage  $E_i$  on the instrument is given by  $E_i = E \frac{R_i}{R_i + R_g}$ . If  $R_i$  is one thousand times  $R_g$ , the instrument measures with a deviation of 0.1 per cent.

In a compensation measurement such as is represented in fig. 4, the potential difference between the input terminals of the instrument will be fully compensated in the equilibrium state. No current then flows through the input resistance and no error occurs. The sensitivity of the instrument does, however, decrease with increasing value of  $R_g$ .

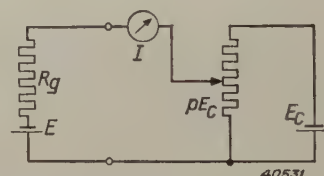


Fig. 4. An apparatus with compensation connections is so adjusted that the instrument  $I$  gives no deviation.  $pE_C$  is then equal to  $E$ . The resistance of the glass electrode results only in a decrease of the sensitivity of the connections. The current  $I$  is equal to  $\frac{pE_C - E}{R_g}$ .

If  $pE_C - E$  is equal to 1 millivolt and  $R_g$  amounts to a million ohms this current is  $10^{-9}$  amperes, thus very small.

- 2) A difference of 0.01 in the  $pH$  value must be observable, while the absolute value must be able to be measured accurately to within several hundreds of a unit. This means that 0.5 millivolt must be observable.
- 3) The influence of temperature changes on the results of the measurement must be eliminated.

There are various possibilities for measuring the potential difference which we shall now deal with in turn.

### Sensitive galvanometer

Good results can in general be obtained by the use of a compensation method with a very sensitive galvanometer. Such galvanometers are, however, so delicate that they are only seldom used in practical cases. Moreover, care must then



also be taken that the resistance in the glass electrode is not too high. Kinds of glass could be chosen for this purpose with very low specific resistance, but from a chemical point of view those glasses are much less resistant than the Corning glass 015 ordinarily used for glass electrodes.

### Direct-voltage amplifier

The potential difference can also be amplified immediately or after compensation with a D.C. voltage amplifier, and then measured. In both cases a much sturdier instrument can be used (fig. 5). This method also, however, has two disadvantages. In the first place the current through the instrument varies when the anode current of the amplifier valve changes. The latter changes not only due to the change in the grid voltage of the valves, but also due to changes in the temperature of the cathode, of the structure of the cathode surface and of the contact potential of the grid.

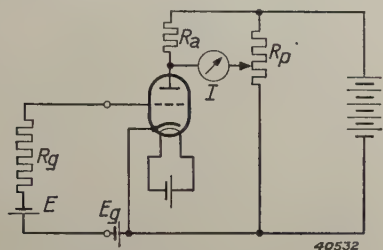


Fig. 5. The voltage  $E$  is fed to the grid of an amplifier valve. For correct adjustment a negative grid voltage is given with the battery  $E_g$ . The anode current of the valve flows through resistance  $R_a$ , so that a difference in voltage occurs over  $R_a$ . The potentiometer  $R_p$  is so adjusted that at a certain value of  $pH$  no current flows through the instrument  $I$ . In the subsequent measurements the current through the instrument is proportional to the deviation of the value of the  $pH$ .

In the second place the input resistance of the valve cannot be high enough compared with the resistance  $R_g$  of the glass electrode. If the valve contains gas residues, these may become ionized and give off charge to the grid. Electrical leakage along the insulation materials and photoelectric current from the grid due to the light from the hot cathode also decreases the input resistance. In a so-called electrometer triode<sup>2)</sup> these disadvantages are indeed avoided, but the result is the disadvantage of only slight sensitivity.

A variation on this method, which has been successfully employed, is the following (fig. 6). With the help of the voltage to be measured a condenser is charged; when the condenser is full, which in micro-analyses may, however, take about a minute, the current is zero. This D.C.

<sup>2)</sup> Cf. also: Philips techn. Rev. 5, 54, 1940.

voltage is then measured with a compensation connection with valve amplifier. The disadvantages which may be mentioned are that here also the variation of the anode current produces a deviation and that the contact of the switch must be closed again each time before a measurement can be carried out.

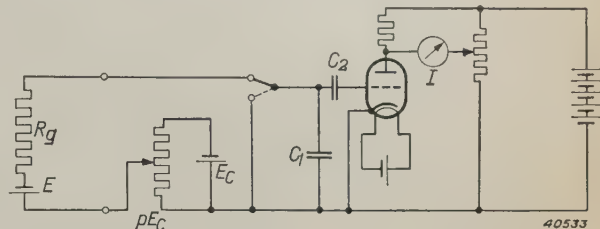


Fig. 6. The connections are largely similar to those of fig. 5. The electrode circuit with voltage  $E$  which is compensated with the voltage  $pE_C$  is reached. The condenser is then suddenly discharged by means of the reversing switch. The changes in voltage are applied to the grid with the condenser  $C_2$ . The current impulse is observed with the instrument  $I$ . As soon as the compensation is complete so that  $pE_C$  is equal to  $E$ , the current impulse will be zero. The voltage  $E$  is read off on the compensator.

### Alternating voltage amplifier

As just explained a D.C. voltage amplifier has several disadvantages. In our apparatus we have attempted to avoid them by first converting the D.C. voltage into an A.C. voltage and then amplifying the latter.

### Description of the apparatus

The  $pH$ -meter GM 4491 contains an electrometer and a compensation part. The latter compensates the voltage between the saturated calomel electrode and the glass electrode. With the electrometer it is possible to ascertain when the compensation is accurate to within 0.5 millivolt. We shall now describe the two parts separately.

#### 1) The electrometer

A condenser is connected to the electrode circuit by a resistance of a high value. When the voltage is  $V$ , the charge  $Q$  of the condenser  $C$  then amounts to:

$$Q = CV.$$

The size of the condenser is varied by allowing the plates to vibrate periodically with respect to each other, charge must then flow back and forth with the same periodicity and an A.C. voltage occurs on the high resistance. If, however, the D.C. voltage is zero no A.C. voltage occurs. The A.C. voltage is amplified and when present made visible with a cathode ray indicator. As an A.C. voltage amplifier this can be made very



stable, and since the A.C. voltage can be fed to the grid with a condenser, except for dielectric losses, the input resistance is infinitely large.

We shall now go somewhat more deeply into the action of the vibrating condenser.

### The vibrating condenser

The electrometer contains a valve oscillator which generates an electrical A.C. voltage of 125 c/s. This electrical energy drives a mechanical vibration system. The latter consists of a shaft bearing a flat plate and a coil and is fastened flexibly with two membranes. The coil is situated in a magnetic field (see fig. 7) and

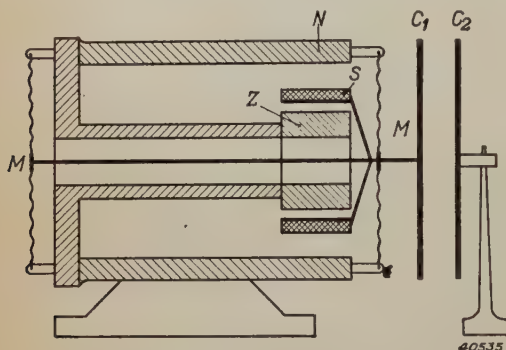


Fig. 7. The vibrating condenser. The condenser plate  $C_1$  is fastened to the end of a shaft which is hung on two membrane springs  $M$ . Through the coil  $S$  fastened to the shaft flows an alternating current of 125 c/s. In the magnetic field between the north pole  $N$  and the south pole  $Z$  the coil experiences an alternating force. The coil with shaft and the condenser plate  $C_1$  begin to vibrate with this frequency. The capacity of the condenser formed by the electrode  $C_1$  and a second electrode  $C_2$  therefore also varies at a frequency of 125 c/s.

begins to vibrate when an alternating current flows. Since the mechanical resonance frequency is equal to the frequency of the A.C. voltage a satisfactorily sinusoidal vibrational state occurs. The vibrating plate, together with a fixed one parallel to it and lying opposite it, forms a condenser whose separation has a sinusoidally varying component and whose capacity thus varies by one third of its value.

In order to obtain a good idea of the sensitivity of the mechanism it is instructive to calculate the electrical system.

At each moment the charge  $Q$  is equal to capacity  $C$  times voltage  $V$ :

$$Q = CV.$$

The current  $i$  is equal to the derivative of the charge with respect to time

$$i = \frac{dQ}{dt} = C \frac{dV}{dt} + V \frac{dC}{dt}.$$

Ohm's law gives the following for  $R$ :

$$\frac{V_0 - V}{R} = C \frac{dV}{dt} + V \frac{dC}{dt} \dots (4)$$

Let the variation of the distance be described by

$(1 + a \cos \omega t)$  times an average value. The capacity then has the form

$$C = \frac{1 + a \cos \omega t}{C_0}.$$

In the apparatus here described  $a$  is about  $\frac{1}{3}$  and  $\omega RC_0$  is equal to 30. This value of 30 is obtained by using a very high value of the resistance  $R$ . This could be realized with a column of liquid which has a resistance of 1000 million ohms.

For a sufficiently high value of  $\omega RC_0$  the approximate solution of the differential equation (4) for the variation in voltage is as follows:

$$V - V_0 = a V_0 \left( \cos \omega t - \frac{1}{\omega RC_0} \sin \omega t \right) \dots (5)$$

Since  $\frac{1}{3}$  of the capacity oscillates and  $a$  is therefore equal to  $\frac{1}{3}$ , and since  $\omega RC_0$  is large enough, namely equal to 30, we may finally use the approximate expression:

$$V - V_0 = \frac{1}{3} V_0 \cos \omega t \dots (6)$$

for the voltage variations without hesitation. An A.C. voltage is thus obtained on the resistance  $R$  whose peak voltage is equal to  $\frac{1}{3}$  of the D.C. voltage to be measured.

The effective value of the A.C. voltage obtained is then  $1/\sqrt{2}$  times this part, i.e. 23 per cent of the D.C. voltage.

It is required that a deviation of 0.01  $pH$  unit should be easily observed. According to the formula already given, this corresponds to a difference in D.C. voltage of 0.58 millivolt. The A.C. voltage amplifier must therefore make observable a voltage of 0.23 times 0.58 millivolt, or 0.1 millivolt.

### Work functions

In addition to the externally applied potential differences there is an internal electromotive force in the apparatus.

The voltage that corresponds to the energy which is necessary to cause an electron to leave a metal surface is called the work function. Two metal objects with different work functions are brought close to each other. If any transport of electrons is possible through the intervening space, the metal with the higher work function will lose fewer electrons than that with the lower work function, until this nonstationary state is compensated with the help of charges on the surface.

The vibrating condenser which has just been described will in general therefore receive a charge. The difference in work function is given, the capacity varies in magnitude, the charge must therefore also vary. Even when the connection terminals of the instrument are short-circuited, therefore, an A.C. voltage will be generated. (This is of course by no means contrary to the main laws of thermodynamics, but means that mechanical energy of the vibrating system is converted into electrical energy). For any two plates of the same material the work function may differ as much as several tenths of a volt. It is found that the effect can be reduced to a few millivolts by using two plates of a very pure metal.

In the apparatus here described this small voltage must be compensated with an externally applied voltage before the apparatus is used. A potentiometer is introduced for this purpose.



### The amplifier

The deviations from the equilibrium state in the case of incorrect compensation are made visible, as already stated, on the fluorescent screen of a cathode ray indicator. These tubes are already familiar as tuning indicators<sup>3)</sup> in modern radio receivers. The important point here is that a voltage of 1 V is easily observed. An amplification of 10000 times is thus necessary. This is possible with two pentode valves in cascade connection (fig. 8). Since an input voltage of

portant to simplify this observation, and a holder has been constructed for this purpose which makes it possible to fasten the removable cathode ray indicator beside the burette, so that attention can be concentrated simultaneously on these different points. The voltages are supplied *via* loose cables.

### 2) The compensator

The compensator offers the following possibilities.

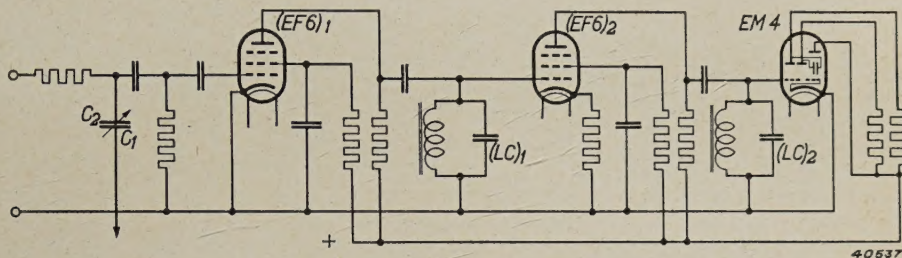


Fig. 8. Diagram of the electrometer. The D.C. voltage to be measured is fed to the vibrating condenser plate  $C_1$ ; this D.C. voltage is compensated by the application of a compensation voltage to the other electrode  $C_2$ . If the compensation is not complete, an A.C. voltage is generated which is applied to the grid of the first pentode  $(EF6)_1$ . The voltage is selectively amplified with the resonance circuit  $(LC)_1$ . With  $(EF6)_2$  and  $(LC)_2$  this is repeated; the cathode ray indicator  $(EM4)$  then makes the A.C. voltage visible.

0.1 millivolt must be readily observable, small noise voltages and voltages from the supply mains may also become visible as interferences. By means of two resonance circuits introduced into the anode connections, only a very small frequency region  $\Delta f$  in the neighbourhood of the oscillator frequency is amplified (fig. 9). As already discussed in this periodical<sup>4)</sup> the noise voltage  $V_R = \sqrt{4kTR\Delta f}$ , or, after substitution of the numerical values,  $V_R = 6 \mu V$ . On the input terminals therefore this voltage may be neglected compared with the quantity to be measured. The resonance frequency of 125 c/s is so chosen that 50 c/s as well as its second and third harmonics, 100 and 150 c/s, fall well outside the resonance region.

In measuring entirely unknown quantities it is important that the sensitivity should be able to be reduced. This is possible since the cathode ray indicator is not equally sensitive in all sectors. At the same time there is also a switch with which a further reduction by a factor of 30 can be obtained.

In the performance of titrations this possibility of less sensitive measuring is also desirable, because in that case the approach to the turning point is clearly seen in advance. It is very im-

- 1) The measurement of the quantity  $pH$  with an electrode of Corning glass 105, with a hydrogen electrode, or with a quinhydrone electrode. As comparison electrode a saturated calomel electrode is used in each case. The previously derived formula (3):

$$\Delta E = E_0 - pH [58.1 + 0.2 (t-20)]. \quad (3)$$

always serves as the starting point for these measurements. The last term containing the

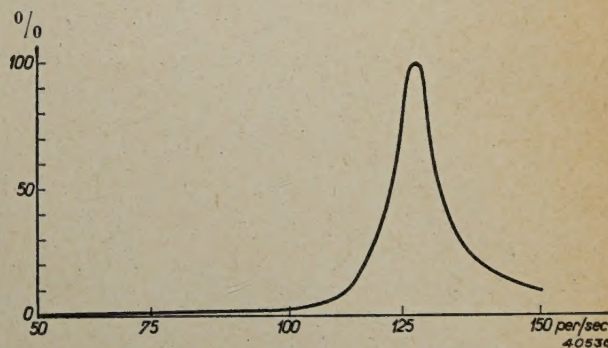


Fig. 9. Characteristic of the A.C. voltage amplifier. In order to eliminate the interference by the supply voltage of 50 c/s and its higher harmonics of 100 and 150 c/s, the amplification is made selective for the oscillator frequency of 125 c/s. The two resonance circuits (fig. 8) are tuned to this frequency. Thus at 50 c/s the amplification is 0.5%, at 100 c/s 2.5% and at 150 c/s 9% of that at 125 c/s. The influence of interference voltages is thus made so small that they fall entirely outside the limit of observation.

<sup>3)</sup> See for example: Philips techn. Rev. 2, 270, 1937.

<sup>4)</sup> Philips techn. Rev. 6, 129, 1941.



temperature  $t$  is taken into account with the help of the potentiometer  $R_3$  between the limits 10 and 40 °C.

2) The performance of voltage measurements on

three steps. A switch with 7 stages of 2  $pH$ -units, a switch with 10 stages of 0.2  $pH$ -unit and the potentiometer  $R_1$  which divides 0.25  $pH$ -unit. In this way an accuracy of 0.02  $pH$ -unit plus 2 per cent of the value measured is obtained over the whole region.

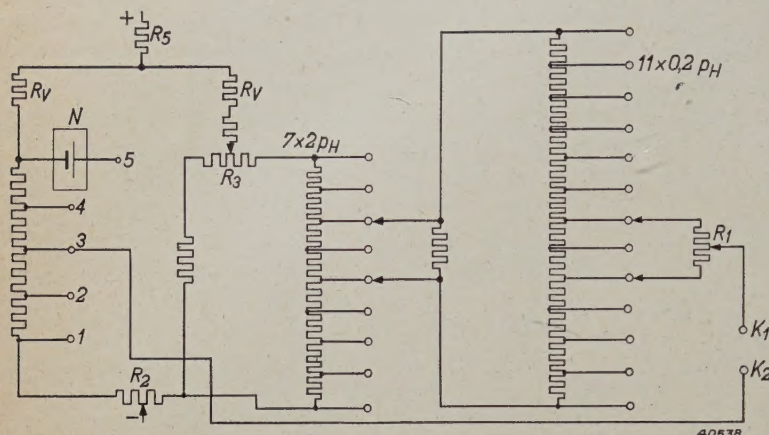


Fig. 10. The compensator. This figure represents the connections as arranged for measurements of the  $P_H$ . By commutation the electrical voltages can be measured in millivolts, or a control measurement with the standard element  $N$  can be carried out. The stabilized D.C. voltage of the supply is connected between  $+$  and  $-$ . The compensation voltage is connected at the terminals  $K_1$  and  $K_2$  with the plate  $C_1$  of fig. 8. The voltage distributor is constructed in three stages and calibrated in steps of 2 and 0.2  $P_H$  units, respectively, the potentiometer  $R_1$  in 25 scale divisions of 0.01  $pH$  unit. The constant voltage  $E_0$  in formula (3) is compensated by connecting the voltage distributor to the terminals 1, 3 and 4, respectively. Position 2 serves for the measurement in millivolts, position 5 for the control measurement, which is not dealt with in detail in this description. A small difference in voltage can be produced with the potentiometer  $R_2$ , by means of which the difference in work function of the electrometer condenser and the so-called asymmetry potential of the glass electrode may be compensated. The potentiometer  $R_0$  is calibrated in degrees Centigrade. A shift of the contact results in a change of the voltage on the voltage distributor which is calibrated in  $pH$  units. The variation of the term  $[58.1 + 0.2(t-20)]$  is realized in this way. The large resistances  $R_0$  provide that the variation of the potentiometer  $R_0$  shall not affect the constant voltage of the terminals 1, 3 and 4,  $R_0$  is a series resistance for the regulation of the input voltage.

a source of voltage with either the positive or the negative pole earthed. Between 0 and 1425 mV the voltage can be adjusted to within 1 millivolt per scale division with the switches and the potentiometer. The accuracy of this voltage measurement is determined by the precision of the resistances of the compensator connections and amounts to 1 mV plus 2 per cent of the value measured.

A few striking points in the construction of the compensator are given below.

- All the important resistances are wound on a ceramic core of metal wire having a low temperature coefficient. After having been subjected to great temperature differences for a long time (aged) they are made accurate to within 0.05 per cent.
- In order not to depend upon a continuously adjustable potentiometer which is by nature fairly inaccurate, the reading takes place in

moist the holder can be taken out and the silica gel dried at 140 °C.

The whole apparatus is shown in fig. 11.

### The chemical part

Since an electrical instrument should be kept away from apparatus which makes use of chemical reagents, the chemical apparatus is housed in a separate box, whose cover can be used as a measuring box (see fig. 12). A rod with a clamp can be fastened into the cover and used as support. A short description of the mechanical construction of the glass and the calomel electrodes and of the principle of the buffer solution follows below.

#### 1) The glass electrode

Since the resistance may be high, the wall is several millimetres thick, giving a very sturdy unit (fig. 13). Care is taken that the potential differences due to differences in the internal

- The compensator connections are fed from the A.C. mains. After rectification the voltage is stabilized with a gas-filled stabilization tube. This tube keeps the voltage accurately constant within 1 per thousand for several hours. In the course of a year the voltage may vary by several per cent. The voltage of the stabilization tube is regularly checked with a saturated standard element according to Weston and any deviation is eliminated with the series resistance  $R_1$ . The standard element produces no current; no battery or accumulator which has a limited life or must be charged is thus used in the apparatus.

d) The difference in work function of the condenser plates can be compensated with a potentiometer.

e) The whole apparatus is made as tight as possible against moisture with rubber and felt. Granular silica gel containing a cobalt salt as moisture indicator serves as drying agent. If it is observed through the window that it is





Fig. 11. The apparatus is built into a metal box which is made moisture tight. An opening covered by a magnifying lens for the cathode ray indicator may be seen. Above it is a second window giving access to a quantity of silica gel as drying agent. By using a strong baked lacquer, by chromium plating certain parts and by making it very tight against moisture, every attempt has been made to make the instrument suitable for use in chemical laboratories. Further protection is given by a heavy wooden case.

and external surfaces are smaller than ten millivolts. The electrode is filled with 0.1 normal HCl solution. This combination has a very low temperature coefficient for the internal voltage difference.

## 2) The saturated calomel electrode

In *fig. 14* it may be seen that the internal part is fused into a tube only 6 mm in thickness. By means of a piece of porous stone the space containing platinum wire, mercury and calomel is in contact with the surrounding reservoir containing saturated KCl solution. The advantage is that this part is very well protected mechanically and chemically, making the cleaning and filling of the KCl container very simple. It is still further simplified by the fact that the electrode can be taken apart (*fig. 15*).

When a small quantity of the liquid to be measured penetrates into the capillary there is a danger that the KCl solution will be contaminated. By means of the small stopcock at the end of the side tube a bubble of air is then admitted, a drop of KCl then escapes and the capillary is rinsed clean in this way.

## 3) Buffer solutions

It is desirable at certain intervals to carry out a *pH* measurement of a liquid having a known hydrogen ion concentration in order to check the correctness of the indications of the measuring electrodes. Such liquids are realized in the form of so-called buffer solutions. These are solutions of measured quantities of acid with a quantity of a salt, which possess the property that their *pH* value is very insensitive to slight contaminations by acids or bases which are either already present in the water or go into solution from the glass. Kolthoff has given a method of preparing such mixtures in tablet form. A tablet dissolved in 20 cm<sup>3</sup> of water gives a good buffer solution suitable for checking the electrode circuit, and if necessary correcting it. Three tubes with twenty tablets for the *pH* values 3, 6 and 8 are included in the apparatus.

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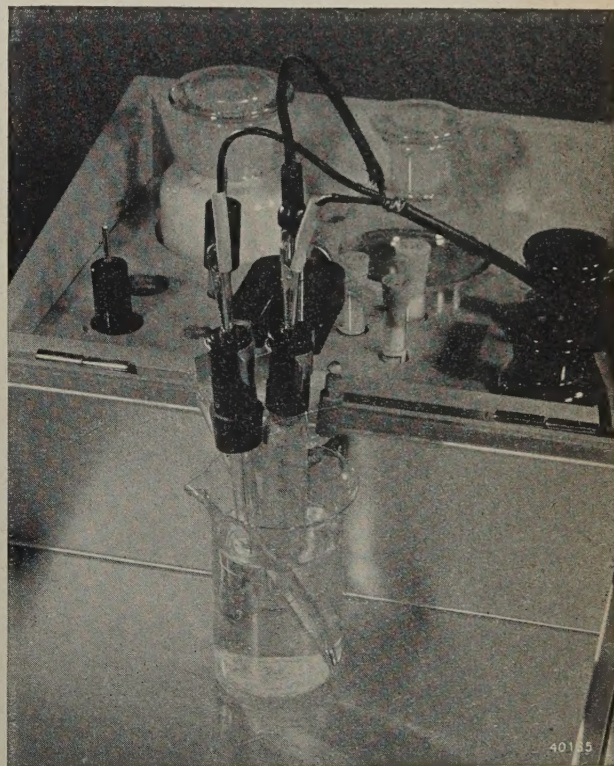


Fig. 12. The chemical part of the apparatus is housed in a separate wooden case. Two glass electrodes, a calomel electrode, platinum electrode and thermometer, bottles with buffer tablets for the *pH* values 3, 6 and 8, potassium chloride and quinhidrone and a set of beakers all have places in the case. In order to make measurements possible even outside the laboratory the cover of the case is constructed as a measuring container. In the photograph may be seen a measuring set-up with standard, clamp and two electrodes.



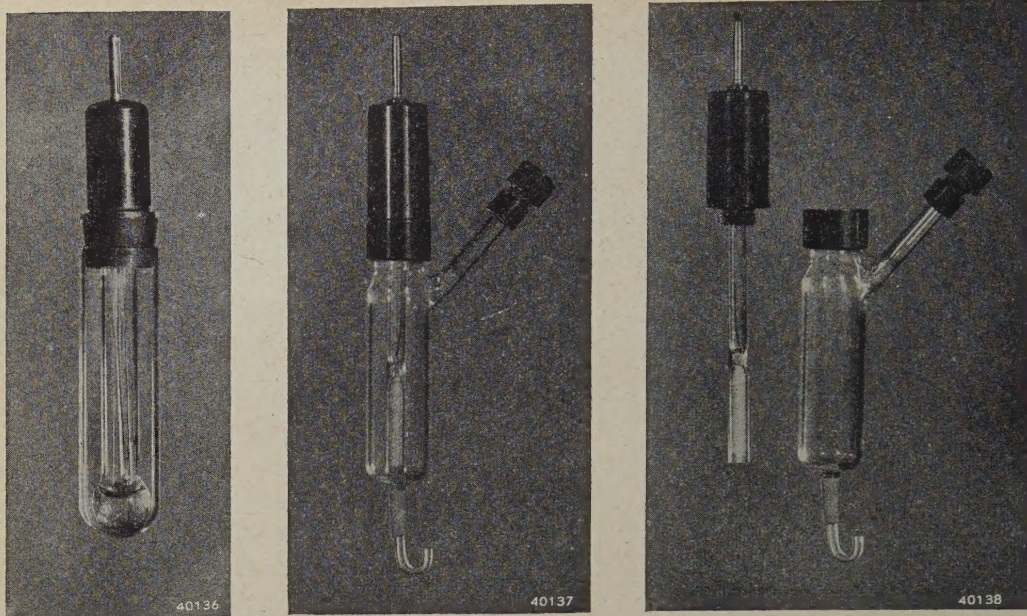


Fig. 13. The *pH*-meter GM 4491 makes it possible to carry out accurate measurements with glass electrodes of very high resistance. The glass electrode shown here has an electrical resistance of 100 million ohms. This value could be obtained with a strong, thick wall of Corning glass 015. The electrode is filled with a buffer solution in which is immersed a silver wire as electrode. The filling is so chosen that the jump in voltage at the silver and at the inside of the glass together have a temperature coefficient which is practically zero.

Fig. 14. A saturated calomel electrode is used as comparison electrode. A space filled with a saturated solution of KCl is connected through a capillary with the liquid to be measured. This solution is connected with an inner electrode through a piece of porous stone. The inner electrode contains a platinum wire immersed in mercury. On the mercury calomel ( $\text{Hg}_2\text{Cl}_2$ ) is formed which makes very good contact with the solution of potassium chloride. Through the stopcock projecting to one side air bubbles can be admitted which push the solution through the capillary and rinse it clean in this way.

Fig. 15. The inner section of the calomel electrode can be taken out of the potassium chloride reservoir. The latter can then be easily cleaned and filled; in case of breakage this simple outer section can be replaced.

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